EVALUATION OF FIXED CHARGE DENSITY AND TRANSPORT PHENOMENA IN INORGANIC PRECIPITATE MEMBRANES

ABSTRACT
THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

CHEMISTRY

By

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DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
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ABSTRACT

This thesis entitled, ***"Evaluation of fixed charge density and transport phenomena in inorganic precipitate membranes"***, deals with the preparation and electrical potential measurements of titanium, vanadium and titanium–vanadium phosphate membranes.

The membrane can be defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid, can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 100 micron to several mms. The properties of membrane materials are directly reflected in their end applications. Some criteria for their selection are mechanical strength, temperature resistance, chemical compatibility, hydrophobicity, hydrophilicity, permeability, permselectivity and the membrane material as well as manufacturing process.

The technological development of inorganic membrane processes for hemodialysis, hemofiltration, gas separation, producing oxygen enriched air, controlling air and water pollution, environmental monitoring, harnessing of solar energy, nuclear reactor, pulp and paper industry, exploring oil and gas reservoir, chemical technology, ion–selective electrode, pharmaceutical industries, biotechnology, classification and separation of food products,

synthesis of acid, bases and organic compounds, petrochemical plants, fuel cell etc.

The sol–gel process is a versatile solution process for making ceramic and glass materials. In general, the sol–gel process involves the transition of a system from a liquid sol into a solid gel phase. It is possible to fabricate ceramic or glass materials by applying the sol–gel process in a wide variety of forms. The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol–gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, or a sol. Further processing of the sol enables one to make ceramic materials in different forms. The sol–gel route involves filtration of viscous sol through microporous support, gelation and sintering. The viscosity of the sol is conditioned by inclusion of a binder and hence, the selection of binder plays a dominant role in the fabrication of membranes. Binders are used to allow the adjustment of sol viscosity and protect thin layer from cracking during sol–gel transition at drying stage. The increase in viscosity was accompanied by a decrease in the surface tension of the binders. Hence a binder with low surface tension in the solution is preferable for good adhesion. Once the membranes are prepared, the next stage is to ensure their mechanical, thermal, chemical stability and surface morphology.

SEM is the type of electron microscope capable of producing high resolution images of a sample surface and the manner in which the image is

created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample. The SEM is a microscope that uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most widely used instruments in research areas today.

Fixed-charge density is the central parameter governing transport phenomena in membranes and depends upon the feed composition and applied pressure and also on the prefential adsorption of some ions of electrolyte on membrane surface. The fixed-charge concept of TMS model for charged membrane is an appropriate starting point for the investigations of the actual mechanisms of ionic or molecular processes which occur in membrane phase. To evaluate this parameter for the simple case of a 1:1 electrolyte and a membrane carrying various charge densities $\overline{D} \leq 1$. The theoretical and observed potentials were plotted as a function of concentrations. Thus, the coinciding curve for various electrolyte system gave the value for the charge density $\overline{D}$ within the membrane phase. The surface charge density $\overline{D}$ of these membranes is found to depend on the applied pressure to which the membrane

was subjected to its initial stage of preparation. It was observed that membranes prepared at lower pressure have low fixed-charge density whereas membrane prepared at high pressure carry higher charge-density and essentially wider and narrow surface openings respectively. The surface charge model works as a tool to improve the performance of the membrane filtration process.

2. Preparation and Surface Charge Density of Titanium Phosphate Membranes for Uni-univalent Electrolyte Solution

The polystyrene-based titanium phosphate membranes were prepared by sol–gel process and found that it is stable and did not show any dispersion in water and in other electrolyte solutions. The theoretical values of membrane potential were obtained by using TMS equation at various concentrations and found to be closer to the experimental values. Therefore, the TMS equation may be utilized for obtaining the membrane potential and the related electrochemical parameters for characterizing of ion–exchange membrane. The transport number and fixed-charge density obtained from membrane potential measurement indicated that the properties of inorganic membrane are similar as that of the commercial ion– selective membrane. The effect of pressure on the prepared membrane have wider pores and essentially low fixed-charge density at lower pressure while carry high charge-density and having narrow surface opening/channel at higher pressure. The surface charge model may work as a tool to improve the performance of the membrane filtration process and the charge property of the membrane dominates the electrostatics interaction

between the membrane and particles in the solution. The transport properties of membrane are also controlled by ion distribution coefficients and the discrepancies in distribution coefficients with varying the concentration of electrolytes is due to the prefential adsorption of some ions on the membrane surface.

3. Preparation and Surface Charge Density of Vanadium phosphate Membranes for Uni-univalent Electrolyte Solution

The polystyrene based vanadium phosphate membrane were prepared by sol–gel route process and found that prepared membranes were stable and did not show any dispersion in water and in other electrolyte solutions. It was observed that membranes prepared at lower pressure have low fixed-charge density whereas membrane prepared at high pressure carry higher charge-density and essentially wider and narrow surface openings respectively. Membrane with higher fixed charged density offered high membrane potential for a given electrolyte solution, and the membrane potential and the distribution coefficient values were observed to be diminished with increasing the electrolyte concentration and their order found to be, KCl > NaCl > LiCl. The experimental values were found to be quite close to the theoretical values. Therefore, it was concluded that the TMS equation may be utilized for obtaining the membrane potential and derived parameters for the membrane under investigation and applicable to other composite membrane.

4. Preparation and Surface Charge Density of $TiPO_4$–VPO_4 Composite Membranes for Uni-univalent Electrolyte Solution

The TVP composite membranes were prepared by sol–gel process, and results indicate that the sol–gel approach is appropriate for composite membrane synthesis. The experimental results were analyzed on the basis of the TMS approach, and it was found that the calculated values agree well with the experimental results at lower concentration region while a little deviation exists at higher concentration region because of the larger deviation of activity coefficients of ions from unity. The fixed-charge density is the central parameter governing transport phenomena in membranes, and it depends upon the feed composition and applied pressure due to the prefential adsorption of some ions and it accounted for altering the charge density and in turn, performance of membrane. The charge effectiveness of the membrane was also greatly influenced form applied pressure and the order for electrolyte is as KCl < NaCl < LiCl, in accordance with increasing hydration radii of the electrolytes within the membrane phase. The mechanical, thermal, chemical satability as well as the ionic transport data of this membrane is similar to that of the conventional membrane and therefore, the TVP composite membrane might be utilized for commercial application.

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Dedicated to

My Ever-loving Parents
&
Ashraf R. Siddiqui

Dr. Rafiuddin
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CERTIFICATE

This is to certify that the thesis entitled **"Evaluation of Fixed Charge Density and Transport Phenomena in Inorganic Precipitate Membranes"**, describes the original work of **Ms. Fakhra Jabeen,** carried out under my supervision and is suitable for submission for the award of Ph.D. degree in Chemistry.

(Rafiuddin)

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Last but not least with all faith in the Almighty I place this work in the hands of my examiner with the hope that he will bear with the shortcomings that might have crept into this thesis inadvertently.

Fakhra Jabeen

(Fakhra Jabeen)

List of Publications

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1. Preparation and Evaluation of Effective Fixed Charge Density of Titanium Phosphate Membranes for Uni-univalent Electrolytes in Aqueous Solutions

   Fakhra Jabeen, Rafiuddin, *J. Sol-Gel Sci. Technol.*, **44** (2007) 195–202.

2. Preparation and Development of Surface Charge Density of Vanadium Phosphate Membrane in Electrolytes Solution

   Fakhra Jabeen, Rafiuddin, *J. Appl. Polym. Sci.*, Reference: APP-2007-05-1373, In Press (John Wiley & Sons)

3. Membrane Potential and Fixed Charge Density across $Tipo_4$–Vpo_4 Composite Membranes for Uni-univalent Electrolyte Solution

   Fakhra Jabeen, Rafiuddin, *J. Porous Mater.*, Springer,
   Available Online: *DOI 10.1007/s10934-008-9195-x*

List of Symbols

Nomenclature

AR	analytical reagent
C_1, C_2	concentrations of electrolyte solution either side of the membrane (mol/l)
C_{op}	optimum concentration
$\overline{C}_{1+}$	cation concentration in membrane phase 1 (mol/l)
$\overline{C}_{2+}$	cation concentration in membrane phase 2 (mol/l)
C_i	i^{th} ion concentration of external solution (mol/l)
$\overline{C}_i$	i^{th} ion concentration in membrane phase (mol/l)
$\overline{D}$	charge density in membrane (eq/l)
F	Faraday constant (C/mol)
$K_{\pm}$	distribution coefficient of ions
80–160 MPa	pressure (Pa)
q	charge effectiveness of the membrane
R	gas constant (j/K/mol)
SCE	saturated calomel electrode
SEM	scanning electron microscope
TMS	Teorell, Meyer and Sievers
TVP	Titanium–Vanadium Phosphate
t_+	transport number of cation
t_-	transport number of anion
$\overline{u}$	mobility of cations in the membrane phase ($m^2/V/s$)
$\overline{U}$	$(\overline{u} - \overline{v})/(\overline{u} + \overline{v})$
$\overline{v}$	mobility of anions in the membrane phase ($m^2/V/s$)
V_k	valency of cation
V_x	valency of fixed charge group

Greek symbols

$\gamma_{1\pm}, \gamma_{2\pm}$	mean ionic activity coefficients
$\overline{\omega}$	mobility ratio
$\Delta\psi_d$	deviation in potential from theoretical value
$\Delta\psi_m$	observed membrane potential (mV)
$\Delta\overline{\Psi}_m$	theoretical membrane potential (mV)
$\Delta\Psi_{Don}$	Donnan potential (mV)
$\Delta\overline{\Psi}_{diff}$	diffusion potential (mV)

CONTENTS

CHAPTER 1

GENERAL INTRODUCTION

The studies of transport phenomena through inorganic membranes have drawn special attention in the field of science and technology during the last few decades [1–3]. Investigators from various disciplines, for example chemists, chemical engineers, biologists, pharmacologists, physists and mathematicians, have made ceaseless efforts and demonstrated significant contribution in these fields although the starting points, views and aims have been quite different. Chemists and chemical engineers utilizing inorganic membranes and their several modified forms have used different parameters to understand the mechanism of transport. The knowledge obtained, might be able to fabricate membranes of any desired property for industrial and other specific uses [4]. Biologists on the other hand tried to use them as a simple model for physiological membranes to understand the behavior, nature and function of extremely complex biomembranes [5]. Pharmacologists however, used the knowledge to understand the controlled delivery of drugs to their respective targets in the human body [6,7]. Physists and mathematicians have also tried to develop new techniques and introduced theories to know the transport mechanism [8,9].

The technological development of inorganic membrane is projecting new dimension to replace biological cell membranes. The combined efforts of chemists, biologists, physists and chemical engineers have achieved considerable success not only in the particular area of artificial kidney, liver, skin [10], desalination of brackish sea water economically but also in the areas of employing various membrane processes for hemodialysis, hemofiltration,

gas separation, producing oxygen-enriched air, controlling air and water pollution, monitoring environment, harnessing of solar energy, nuclear reactor, pulp and paper industry, exploring oil and gas reservoir, chemical technology, ion–selective electrode, pharmaceutical industries, biotechnology, classification and separation of food products, synthesis of acid, bases and organic compounds, petrochemical plants, fuel cell and model of theoretical studies etc. [11–16]. Recently, research and development of inorganic membranes for practical uses have been rapidly growing and contributing remarkably for a variety of day-to-day problems related to economic prosperity and physical well-being of man kind.

Due to the fast advancement of membrane technology, the extensive research work on membrane is being carried out in different institutions, research centers, industries and technological establishments all over the world. As a result, every year a number of national and international conferences, workshops, symposia and seminars are being held frequently, resulting in exponential growth of publications in the form of papers, reviews, articles and monographs on different aspects of membrane phenomena has been published [17–20]. A number of research journals of international repute, for example, *Journal of Membrane Science, Separation and Purification Technology, Desalination, Sol–Gel Science and Technology, Applied Polymer Science, Polymer Science, Polymer Research, Colloids and Surfaces, Colloid and Interface Science, Colloid Polymer Science, Water Research, Nature, Porous Materials, Applied Composite Material, Advanced Composite Material,*

Thermochimica Acta, Biochimica et Biophysica Acta, Electrochimica Acta, American Chemical Society, Faraday Transaction, Langmuir, Non–Crystal Solids, Non–Equilibrium Thermodynamics, etc., contain the recent developments in the membrane research field.

The literature concerning membrane is enormous and, in fact, too extensive to mention. The principal volumes containing significant sections devoted to membrane electrochemistry are by *Clarke and Nachmanshon [21], Helfferich [22], Spiegler [23], Merten [24], Marinsky [25], Stein [26], Cole [27], Lakshminarayanaiah [28], Hope [29], Arndt and Roper [30], Plonsey [31], Kotyk and Janacek [32], Keller [33], Parlin and Eyring [34], Caplan and Mikuleeky [35], Eisenman [36], Sandblom and Ome [37], Harris [38], Schlogl [39], Bitter [40], Krikwood [41], Jirikoryta [42], Katchalsky and Curran [43], Danielli, Rosenberg and Cadenhead [44], Ramirez and Mafe [45], Woermann [46], Wagner [47], Harred and Owen [48], Manzanares and Kontturi [49], Chilcott and Coster [50], Finkelstein [51], Haase [52], Debye [53] , Bandini [54], Bowen and Mohammad [55], Ahmad [56], Yamamoto, Matsumoto and Tanioka [57], Chou [58], Aleman and Dickson [59], Tongwen [60] etc.*

A precise and complete definition of the word *membrane* is difficult to propose. In view of the progresses made, leading investigators of *membrane* science and technology proposed the definition of *membrane* as a phase or structure interposed between two compartments, which obstruct or completely prevent gross mass movement between the two, but permits passage with various degrees of restrictions for one or several species of particle from the

two adjacent phases or compartments, and thereby acting as a physiochemical machine that transforms various degrees of efficiency according to its nature and the composition of the two adjacent compartments. In simple term it is described as a phase, usually heterogeneous, acting as a barrier to the flow of molecular and ionic species present in the liquid and/or vapors contacting the two surfaces. According to Lonsdale's viewpoint, a *membrane* is not just an object that obstructs but its definition must embody its function [61]. A *membrane* is a thin wall made of materials that provide an unequal resistance to the transport of different molecules. The molecules are driven across the *membrane* by forces arising from imposed chemical or electrochemical potential gradients. Such potential gradients may be induced within the film by inserting the *membrane* between two media differing in pressure, temperature, composition and electric potential.

Membranes may be broadly classified on the basis of its origin as either natural or artificial. A natural *membrane* is a highly complex, integrated system of lipid, protein and carbohydrates. Natural *membranes* are thin (75–100 A°) trilaminar structures. They consist of two layers of phospholipids having thickness 40–60 A°, sandwiched between two surface-active layers of protein molecules. The former remain linked with each other by inner lipid ends, which are nonpolar and hydrophobic in nature. The external face of the double layer is made up of phosphate ends, which form the polar and hydrophilic ends of phospholipids molecules. Hydrogen bonds, ionic linkages or electrostatic forces bind the molecules of phospholipids and protein together. The proteins

provide elasticity and mechanical strength/resistance to natural *membrane*. A natural *membrane* is a barrier used by nature to maintain physiochemical activities in every cell. The initial conditions are essential for the performance of its function in life itself. In living organisms, the *membrane* fulfill the role of separating two regions and acting as a barrier that closes and opens according to the need of the cell. In addition, biomembranes are invariably more or less charged due to the presence of carbonyl−, amino−, and other fixed-charge groups and hence act as selective barriers between the cell contents and their external environment. It is interesting to note that material transport across biomembrane takes place under the influence of electrical forces. Surprisingly, all *membranes* are permeable to H_2O, O_2 and H_2 and hence these are transported across the *membrane* freely but meticulously controlled.

The proper choice of a *membrane* should be determined by the specific application and objective: particulate or dissolved solids removal, hardness, reduction or ultra-pure water production, removal of specific gases/chemicals, etc. The end use may also dictate selection of *membranes* for industries such as potable water, effluent treatment, desalination or water supply for electronics or pharmaceutical manufacturing, and so on. The following section briefly explains the types of *membranes* commonly used.

1.1 Types of Membranes

1.1.1 *Heterogeneous and Homogeneous Membranes*

The terms *heterogeneous* and *homogeneous* are frequently used in membrane study. The term *heterogeneous* has been used to indicate the internal physical structure and external physiochemical performance [62]. From this point of view, most membranes, in general, are to be considered *heterogeneous*. These membranes are prepared by embedding colloidal ion–exchanger particles in an inert binder which provide sufficient mechanical strength. A necessary requirement for *heterogeneous* membranes are that the ion–exchange particles be in contacts with one another rather than be separated by the binder. Thus the volume percentage of ion–exchanger material should be as high and compatible with the required mechanical strength.

Homogeneous membranes can be prepared by condensation/ polymerization of monomers on mercury or acid-resistant plates or by heating a precondensed, viscous reaction mixture between glass plates. Despite the fact that conventional membranes prepared from coherent gel have been called *homogeneous*. *Heterogeneous* membranes can be made from almost any ion–exchanger, where as the materials from which *homogeneous* membranes can be prepared are rather restricted. However, the properties of *heterogeneous* membranes are not ideal; the electrical conductivity is lower and the permeability for an electrolyte is higher than those of the *homogeneous* membranes.

The terms *heterogeneous* versus *homogeneous* proved to be an important distinction in mass transport capacity. In the dilute solution limit, the friction coefficient of mass transport by diffusion or migration is inconvertible by Onsager reciprocal relation, and both can be related to jump distance and frequencies according to the random walk models. As long as there are no preferred regions of low friction in the membranes. The membrane is isotopic on a molecular level and is considered to be *homogeneous*; the uniformity of mesh on a molecular scale is another view of homogeneity. Channel-free solid and liquid membranes are usually *homogeneous*. The two phase's membrane such as solid crystals embedded in nonionic resin are *heterogeneous*.

1.1.2 *Non Porous and Porous Membranes*

Membranes are considered to be *nonporous* or *porous* depending upon the extent of solvent penetration [63]. At the *nonporous* extreme, the membranes that are nonionic and contain negligible transportable species at equilibrium, e.g., ceramic, quartz, antharacene crystal and teflon film, are examples of solid membranes. Organic liquid films such as hydrocarbon and fluorocarbon, are examples of liquid membranes. At the *porous* extreme, the membranes can be solvated and contain components from the outer phases. Inorganic gels are loosely compressed powder in contact with aqueous solution. These materials absorb solvent from the surrounding media and may also interact with other neutral molecules and ionic salts. More widely studied membranes are polyelectrolytes (solid ion–exchanger), aqueous immiscible

organic liquid electrolytes (liquid ion–exchanger), various parchment-supported inorganic precipitate [64], solid ion-conducting electrolytes including silver halide, rare earth fluoride, alkali silicates and alumino silicate glasses. All these material contain ionic or ionizable groups within the membranes, which are capable of transport under diffusive or electric field forces, and these material possess the properties of porosity. Polyelectrolytes tend to swell rapidly by osmotic pressure and uptake the solvent. Liquid ion–exchangers are surprisingly slow to take up of water, while the inorganic salts have no tendency to hydrate, glass membrane are complicated by simultaneous hydrolysis of the polyelectrolyte during uptake of water [65].

1.1.3 *Polymeric Membranes*

Polymeric membranes are well known for their uniformity, chemical stability and control ion–exchange properties. These membranes have significant advantages over conventional membrane, owing to their electrical nature, adhesive property, thermal conductivity, chemical resistivity and biochemical properties. *Polymeric* membranes are important separation devices extensively used as biomedical membranes in applications such as heamodialysis, heamofiltration, reverse osmosis, blood purification, control drug delivery, etc [66]. In a natural kidney, ultrafiltration of the blood occurs through the capillaries leading to the removal of the waste product and purification of blood. In an artificial unit, a membrane-dependent ultrafiltration achieved essentially the same results. Membranes in the form of either flat

sheets or hollow fibers are employed. A synthetic polymer substitute is being experimented with a polyethyleneglycol, block copolymer membrane that can selectively filter [67]. A modified *polymeric* unit has been used as membrane in which oxygenated blood is allowed to flow through membrane barriers which have very high permeablities to both oxygen and carbondioxide. The flow of oxygen, which is maintained at high partial pressure, displaces carbondioxide and thus this unit is accounted for effective purification. Silicon is the best membrane material available and extensively used as a *polymeric* membrane. It has a high permeability to gases and low permeability to water and can also be autoclaved [68]. Synthetic *polymeric* membranes are the crucial compounds of controlled drug delivery system [69]. The advantage of drug delivery in this fashion is that the drug can be maintained at optimum therapeutic concentration in the body over a long period of time. Besides silicon membranes, ethylenevinylacetate copolymers, polyglycollic acid, lactic acid, block copolymer and certain varities of hydrogel have drawn attention. A hydrogel system is based on butylmethacrylate, hydroxyethlenemethacrylate, have been tested for antitumer drug delivery. *Polymeric* membrane also bearing ion–exchange property has the distinction of being the most widely studied system [70].

1.1.4 *Lipid Membranes*

Lipid membrane was introduced as a model of biomembranes known as *lipid* bilayer membrane [71]. *Lipid* membrane could be regarded as the most realistic model in view of the fact that it has the key structural element of all biomembranes. Bilayer *lipid* membrane or its modified system has been widely and quite satisfactorily used for carrying out investigation into a variety of physical, chemical and biological phenomena. These include solar energy transduction and other relevant phenomena such as ion selectivity, antibody–antigen reaction, active transport and photoelectric effects. These membranes are large enough for direct electrical measurements and have been a major tool for studing membrane phenomena although they have some structural and functional limitations such as retention of solvent in bilayer and long term stability, etc.

1.1.5 *Charged and Uncharged Membranes*

The term *charged* and *uncharged* in the membrane literature is usually unsound electrostatically but does provide an intuitive chemical description. A *charged* membrane refers to an electrolyte membrane, viz., solid or liquid ion–exchangers, where the fixed and mobile sites are having the charges. Actually these membranes are quasi electroneutral in their bulk when the thickness is larger compared with the Debye thickness at each interface. Quasi-electroneutrality means that any volume element is larger compared with the distance between ions and the sum of ionic charges. In the literature *uncharged* membranes are those, like cellophanes, with no fixed-charges. This frequently

used literature definition provides no place for liquid layer membranes. These are electrostatically neutral only in the absence of charge carriers and bathing solutions whose salts possess preferential solubility of anion over cation or vice-versa but are usually electrostatically *charged* by an amount of ion of same sign (positive or negative) in normal operation. Thick hydrocarbon membrane, membrane of diphenyl ether, phthalate and sebacate esters are generally neutral in the presence of most bathing electrolyte. They may be *charged* electrostatically, depending on the thickness, in the presence of neutral carrier species that preferentially solubalize ions of one sign (positive or negative). The use of term *charged* and *uncharged* is described the electrolyte and non-electrolyte membranes and have been discussed unless the precise electrostatic interaction is involved [72].

1.1.6 *Fixed Site and Mobile Site Membranes*

The electrolyte membranes are characterized by the presence of charged sites. The sites are either partially or completely ionized depending on the dielectric constant and solvent penetration [73]. If ionic groups for example – SO_3^{2-}, $-COO^{2-}$, $-PO_4^{2-}$ are fixed in the membrane, attached to cation–exchangers, the membrane is considered to possess fixed sites even though protons or metal ions are covalently bonded to these sites. In glass membrane, the fixed sites are $-SiO^-$ and $-AlO^-$ groups, while in anion–exchangers these are $-N^+$ and $-NH_4^+$. The membranes having same fixed charged groups exclude co-ions by electrostatic repulsion. The extent of exclusion is governed by the concentration of external electrolyte and the

magnitude of the charge fixed to the membrane matrix. On the other hand, liquid ion–exchangers that are water immiscible, such as diesters of phosphoric acid, can be viewed as a *mobile site* membrane. The acid is trapped in the organic phase, while the proton and other cations can move in and out of the membrane frame work.

1.1.7 *Inorganic Membranes*

The *inorganic* membrane was first developed and used in large-scale gas separation processes in 1940. New processes and techniques in *inorganic* membrane technology have been revolutionizing the chemical industry in recent years and acting as substitute of polymeric membrane [74]. *Inorganic* membranes exhibit unique physical and chemical properties compared to other membranes. They can be significantly used at higher temperatures with better structural stability without swelling or compaction. Generally, they can withstand harsh chemical environment without undergoing microbiological attack. They possess very high resistance towards acid and have remarkably high selectivity [75]. Due to their ability to remain stable at relatively high temperature, to resist degradation, fouling, to remain stable under corrosive and oxidizing conditions and are extensively used in separation processes. Their high electrical conductivity and better current efficiency have been used in cells for the electrolyte, desalting of brackish water [76], fuel cell and electrical storage batteries [77]. The *inorganic* ion–exchange membranes are useful in a variety of selective separation processes such as water purification, catalyst recovery, solvent cleanup, food and beverage processing. However, they have

made little headway as a model for biological membranes in spite of the fact that comparatively simpler *inorganic* systems made up of amino, imido and phosphate groups comparable to phospholipids can be investigated and subsequently synthesized.

Two types of *inorganic* membranes are generally known: (i) crystalline and (ii) amorphous. Heteropolysalts such as phosphomolybdates, aminosilicates, etc., belong to the former category, and simple and mixed hydrous oxides of group IV, V and VI belong to the latter category. Ceramic membrane is the another recent development of *inorganic* membrane system and probably the most attractive system for gas separation processes [78] due to its high-molecular sieve-like selectivity and high stability at enhanced temperature (300−1000°C) and are chemically quite stable. Ceramic membrane is used in membrane reactor. It uses catalytically active or passive membrane and is proved to be very promising. Amorphous-type *inorganic* membranes have not been used extensively in practical and industrial purposes. In order to obtain both categories of membranes as sheets of sufficient mechanical strength, they are amalgamated with polystyrene [79]. The parchment-supported membranes have also been employed for this study [80]. *Inorganic* membranes are versatile; they can operate at elevated temperatures, with metal membranes stable at temperature ranging from 500−800 °C and with various ceramic membranes usable over 1000 °C. They are also much more resistant to chemical attack. A variety of materials have been used in the fabrication of *inorganic* membranes and manipulate their features according to the necessity

that is resistance to corrosive liquids and gases, mechanical and thermal stability, etc. *Inorganic* membranes compete with organic membranes for commercial use and in many of the harsh operational environment; organic membranes do not perform well or remain stable and therefore the *inorganic* membranes offer needed solutions.

1.1.8 *Ion–Exchange (Ion–Selective) Membranes*

Ion–exchange (ion–selective) membranes allow selective transport through the membrane of ions or molecules carrying a certain electric charge. The properties of *ion–exchange* membranes are closely related to those of ion–exchange resins, but the purpose of these membranes is not the exchange of ions. When used in processes driven by electrical potential gradient, they enable controlled and selective transport of ions through the membrane. An *ion–exchange* membrane is a foil or a plate made of an *ion–exchange* substance, which is usually a synthetic resin or a macromolecular substance, containing firmly bound (fixed) functional groups with a charge that dissociates when in contact with water or ions. These *ion–exchangers* have the characteristics of a polyelectrolyte with ionized groups bound to the polymeric structure of the membrane. The charge of fixed functional groups in the membrane must be compensated by an equivalent number of oppositely charged ions. They are not fixed by means of covalent bonds and can move freely through the polymeric network until equilibrium of charges is reached. These mobile ions are called 'counter-ions', and the membrane is selectively

permeable for them. Irregular distribution of bound functional groups in a polymeric skeleton of the membrane causes irregularities in the uniformity of spatial charge. These irregularities allow a passage of 'co-ions', i.e. ions with a charge identical to that of the functional groups in the membrane. From the perspective of the physical structure of the membrane, these polymeric *ion–exchange* membranes are heterogeneous and their structure is characterized by *ion–exchange* materials dispersed in an inert polymeric carrier. This offers a broad scope of possible production technologies. An important factor in the attainment of high efficiency of the membranes is the uniform distribution of the *ion–exchange* materials in the inert binder. An *ion–exchange* membrane can be represented in a simple way by a homogeneous model, as shown in Figure 1. Three basic types of *ion–exchange* membranes can be distinguished relative to the nature of the fixed functional groups: (1) Cation–exchange membranes (CMs) which contain firmly bonded acid anionic groups, such as $-SO_3^{2-}$, $-COO^{2-}$, $-PO_4^{2-}$, $-AsO_3^{2-}$, etc., that allow passage of positively charged ions only, since passage of negatively charged ions is considerably restricted. (2) Anion–exchange membranes (AMs), which contain fixed basic cationic groups based on quaternary ammonium groups $-NR_3^+$ (where R is the hydrogen or alkyl group) that allow free passage for negatively charged ions only, since passage of positively charged ions is highly restricted. (3) Bipolar membranes (BMs) that are a combination of CMs and AMs, thus containing both functional groups.

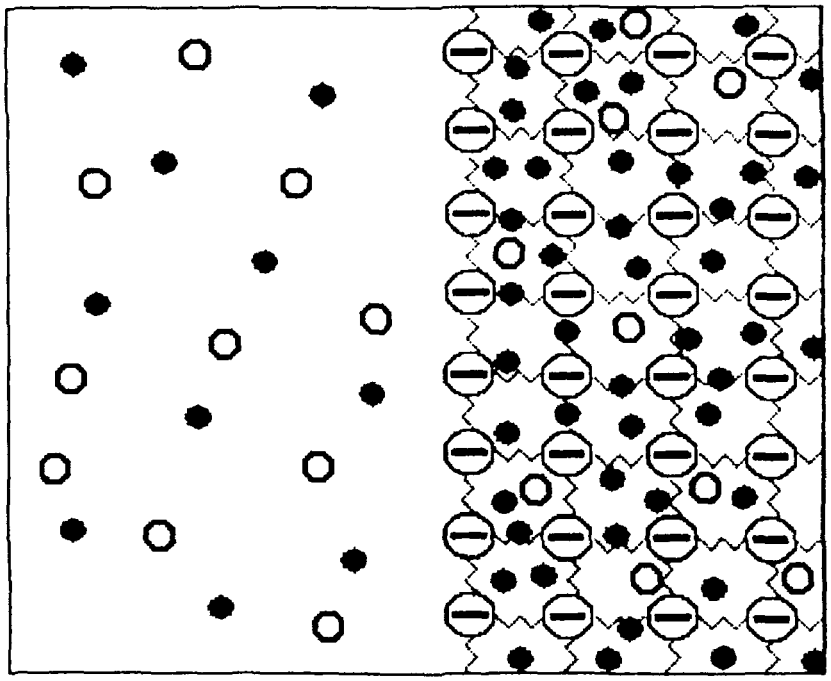

Figure 1. Homogeneous ion-exchange charged membrane immersed in a solution of binary electrolyte [⊖ : fixed charges (in this case negatively charged), ● : Cations, ○ : anions].

Bipolar membranes are composed of two layers of membrane materials, each containing one type of functional group. The membrane layers are bound together using an 'intermediate zone' of 2–5 μm thickness between the layers of the membrane. The BMs are a source of H^+ and OH^- ions that are produced in the intermediate zone by water dissociation. The majority of *ion–exchange* membranes have low selectivity for ions of one specific (i.e., positive or negative) charge. To increase the membrane's ion selectivity, the thin (0.1–1.0 μm) layer of a membrane surface can be modified to act as an energy barrier, which enhances the passage of similar charged counter-ions [81]. Modification of the membrane surface may include etching and deposition of a polymeric *ion–exchange* layer with an opposite electric charge and various other methods.

1.1.9 *Inorganic–Organic (Hybrid) Ion–Exchange Membranes*

Inorganic–organic composite materials are increasingly important due to their extraordinary properties within a single molecular composite, which arise from the synergism between the properties of their components [82]. These materials have gained much interest owing to the remarkable change in their properties, such as mechanical [83], thermal [84], electrical [85] and magnetic [86], compared to pure organic polymers or inorganic materials. In these materials, organic materials offer structural flexibility, convenient processing, tunable electronic properties, photoconductivity, efficient luminescence and the potential for semiconducting and even metallic behavior.

Inorganic compounds provide the potential for high carrier mobilities, band gap tunability, a range of magnetic and dielectric properties and thermal and mechanical stability. In addition to combining distinct characteristics, new or enhanced phenomena can also arise as a result of the interface between the organic and inorganic components [87–89]. Among the many possible applications of inorganic–organic materials, membranes with various compositions and properties are now being prepared from these materials, especially *inorganic–organic (hybrid)* ion–exchange membranes prepared from *inorganic–organic* ion–exchange composite materials. These membranes have received remarkable attentions in recent years. Ion–exchange *inorganic–organic hybrid* membranes can be made by several routes including sol–gel process, intercalation, blending, *in situ polymerization,* molecular self-assembling, but probably sol–gel process is the most prominent one. Kogure *et al.* [90,91] used this method to prepare a hybrid anion–exchange membrane by sol–gel or liquid coupling process of silane coupling agents. Through coupling with these agents to silanol group on the surface of silica membranes, the hybrid membranes become insoluble. Further, the inorganic membranes can give enough mechanical strength to the hybrids [91]. The analogous preparation of a hybrid cation–exchange membrane was also reported by the same research group [90,92]. Hybrid cation–exchange membranes have received more attention compared to hybrid anion–exchange membranes because the thermal stability of the latter membranes permits them to be used as fuel cell separator [93–101].

1.2 Membrane Separation Technology

A membrane separation system separates an effluent stream into two sub-streams known as the permeate and the concentrate. The permeate is the portion of the fluid that passes through the semi-permeable membrane, whereas the concentrate stream contains the constituents that are rejected by the membrane.

A wide variety of membrane separation processes exist. These differ from one another in the type and configuration of the membrane, the mechanism of transmembrane transport for various water solution components, the nature of the process-driving force and other features. While some processes are well proven in full scale industrial applications, others are experimental, in development, or are in transition from the development stage to industrial use. The proven processes have been used for purification, desalination, ion separation, material recovery, or concentration process functions in industries such as water purification, waste-water treatment, pharmaceutical, medical, microelectronics, chemical processing, food processing, etc.

Membrane separation process enjoys numerous industrial applications with the following advantages:

- It causes appreciable energy savings
- It is environmentally benign
- It is a clean technology with operational ease
- It replaces the conventional processes like filtration, distillation, ion–exchange and chemical treatment systems
- It produces high-quality products
- It has greater flexibility in designing systems

Membrane separation processes may be classified and categorized by a number of criteria. An exhaustive variety of membrane classifications can be found [102,103]. A basic distinction between the individual methods lies in the use of the process driving force to purify or concentrate a solution, which may be a pressure gradient (P), concentration gradient (C), electrical potential gradient (E) or temperature gradient (T). In some instances, and specifically in some processes under development, more than one driving force may be used. Membrane processes can be classified as follows with respect to the process driving force:

Pressure gradient (P) as the process driving force:

- Reverse osmosis
- Nanofiltration
- Ultrafiltration
- Microfiltration

Electrical potential gradient (E) as the process driving force:

- Electrodialysis
- Electrodialysis with application of liquid organic membranes
- Membrane electrolysis

- Electrosorption
- Electrofiltration
- Electrochemical ion–exchange

Concentration gradient (C) as the process driving force:

- Dialysis
- Membrane extraction
- Supported liquid membrane (SLM)
- Emulsion liquid membrane (ELM)
- Non-dispersive solvent extraction with hollow fibre contactors
- Pervaporation

Temperature gradient (T) as the process driving force:

- Membrane distillation
- Thermo-osmosis

Processes with combined driving forces:

- Electro-osmofiltration (P + E)
- Electro-osmotic concentration (E + C)
- Gas separation (P + C)
- Piezodialysis (P + C)

A simplified overview of the common membrane separation method arranged by the main process driving force and the respective application range [104] is provided in Table 1.

1.3 Synthesis of Inorganic Membrane by Sol–Gel Process

A *sol* is a dispersion of the solid particles (~ 0.1–1.0 μm) in a liquid where only the Brownian motion suspend the particles. A *gel* is a state where both liquid and solid are dispersed in each other, which presents a solid

Table 1. Membrane Separation Processes: Operating Principles and Applications

Separation process	Membrane type	Separation method	Range of application
Microfiltration	Symmetric microporous membrane	Sieving mechanism as a function of pore size and adsorption	Sterile filtration clarification
Ultrafiltration	Asymmetric microporous membrane	Sieving mechanism	Separation of macromolecular solutions
Nanofiltration	Asymmetric 'skin type' membrane	Solution diffusion mechanism	Separation of divalent ions from solutions
Reverse osmosis	Asymmetric 'skin type' membrane	Solution diffusion mechanism	Separation of salt and microsolutes from solutions
Dialysis	Symmetric microporous	Diffusion	Separation of salt and microsolutes from macromolecular solutions
Electrodialysis	Cation and anion exchange membranes	Selective transport of ions or molecules according to electric charge	Desalting of ionic solutions
Supported liquid membrane	Microporous membranes supporting adsorbed organic liquid	Solution diffusion via carrier	Separation and concentration of metal ions and biological species
Membrane distillation	Microporous membranes	Vapour transport into hydrophobic membrane	Ultrapure water concentration of solutions
Pervaporation	Asymmetric membrane	Solution diffusion mechanism	Separation of organics

network containing liquid components [105–107]. The sol–gel process is a versatile solution process for making ceramic and glass materials. In general, the sol–gel process involves the transition of a system from a liquid *sol* into a solid *gel* phase. Applying the sol–gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultra-fine or spherical-shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials. The starting materials used in the preparation of the *sol* are usually inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol–gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension or a *sol*. Further processing of the *sol* enables one to make ceramic materials in different forms. Thin films can be produced on a piece of substrate by spin-coating or dip-coating. When the *sol* is cast into a mold, a wet *gel* is formed. With further drying and heat-treatment, the *gel* is converted into dense ceramic or glass articles. If the liquid in a wet *gel* is removed under a supercritical condition, a highly porous and extremely low-density material called *aerogel* is obtained. As the viscosity of a *sol* is adjusted into a proper viscosity range, ceramic fibers can be drawn from the *sol* and uniform ceramic powders are formed by precipitation [108,109].

The development of membrane technologies have introduced membrane materials that are prepared from ceramic materials. They offer many potential advantages over commercial organic polymer membranes for separation

processes. Inorganic membranes are very resistant to a wide variety of solvents and are quite stable at hard-operating conditions. These features have attracted a great deal of attention from the standpoint of membrane applications. Among the methods of preparation developed, the sol–gel process is appropriate to elaborate thin and porous layers with controllable porosity. The synthesis of *gel* is based on hydrolysis condensation reactions indirectly to form a variable lattice of oxide from molecular precursors. The hydrolysis reaction must be controlled to avoid precipitation of hydrous metal oxide. A true oxide network is formed by chemical bonds in the solution. The control of sol–gel transition and thermal decomposition has allowed us the synthesis of the mixed oxide ZrO_2–SiO_2. These results show the great potentiality of inorganic membranes and allow new applications to be taken into account, particularly, waste water treatment and gas separation.

1.4 Role of Polymer in Membranes

There are a large number of potential applications of polymer membranes for gas separation; relatively few of them have become applied in practice. The potential application of a polymer as a separation membrane depends upon the permeability coefficient of the gas that is transported more rapidly and whose selectivity is as large as possible. In the past 20 years, the control of gas permeability and permselectivity of polymer membranes has become a subject of strong research with worldwide participation in both industrial and academic laboratories. To achieve such control, it is necessary to

have a good understanding of the relationship between the properties of the polymers and their gas transport properties [110–116]. There do not appear to be any polymers that show the desired trend to a large value for both permeability and selectivity and thus expanding the performance is one goal of current research efforts. In recent years, efforts and successes in synthesizing a variety of nanostructured materials have provided a new degree of freedom for the development of advanced materials with enhanced or novel properties. Nanocomposites represent the current trend in developing novel nanostructured materials. They can be defined as a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale regime [117].

There are several routes to synthesize membranes like anodic oxidation, thin film deposition, sol–gel etc. The sol–gel route involves filtration of viscous *sol* through microporous support, gelation and sintering [118]. The viscosity of the *sol* is conditioned by inclusion of a binder and hence the selection of binder plays a dominant role in the fabrication of membranes. Binders are used to allow the adjustment of *sol* viscosity and protect thin layer from cracking during sol–gel transition at drying stage. Nitrogen containing groups, hydroxyl and methylol, promote adhesion to inorganic and organic adherent. Based on these criteria, polyvinyl alcohol, polyacrylamide and polyethyleneimine were chosen as binders [119]. The increase in viscosity was accompanied by a decrease in the surface tension of the binders. Hence a

binder with low surface tension in the solution is preferable for good adhesion [120].

The polymers most commonly used for the production of membranes are as follows:

- Polystyrene
- Polystyrene sulfonic acid
- Polyvinyl chloride
- Polysulphone
- Polyamide/polysulphone TFCs
- Polyvinyl alcohol
- Polyacrylamide
- Polyethyleneimine
- Cellulose acetate
- Cellulose ester etc

Polystyrene is a polymer made from the monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum by the chemical industry. At room temperature, polystyrene is normally a solid thermoplastic and can be melted at higher temperature for molding or extrusion, then resolidified. Styrene is an aromatic monomer, and polystyrene is an aromatic polymer. Pure solid polystyrene is a colorless, hard plastic with limited flexibility. Polystyrene is economical and can be transparent or can be made to take on various colors. The chemical makeup of polystyrene is a long-chain hydrocarbon with every other carbon connected to a phenyl group (an aromatic ring similar to benzene). A 3-D model would show that each of the chiral backbone carbon lies at the center of a tetrahedron with its four bonds

pointing towards the vertices. Let the –C–C– bonds are rotated so that the backbone chain lies entirely in the plane of the diagram. From this flat schematic, it is not evident which of the phenyl (benzene) groups are angled towards us from the plane of the diagram and which ones are angled away as shown in Figure 2.

1.5 Fixed-Charge Density of Membranes

Several theories have been formulated for the electrical potentials arising across membranes of high fixed-charge density. These may be grouped into three categories: (1) the idealized concept of *Teorell, Meyer and Sievers* (TMS) [121–125] theory and the various refinements of it, notably by *Marshall and Schlogl* [126–130] (2) the pseudo-thermostatic treatment of *Scatchard* [131] and (3) that based on the thermodynamics of irreversible processes, as expounded by *Kirkwood* [132] *Staverman* [133] and others *Lorimer et al.* [134] *Kobatake* [135] *Spiegler* [136]. When a membrane is brought into contact with an aqueous electrolyte solution, the charges are developed on it. It acquires an electric charge through several possible mechanisms, which include dissociation of functional groups; adsorption of ions from solution; and adsorption of polyelectrolyte, ionic surfactants and charged macro-molecules. This charging mechanism can take place on the exterior membrane surface in the same way as on the interior pores surface of the membrane. These surface charges have an influence on the distribution of ions in the solution due to the requirement of the electroneutrality of the system.

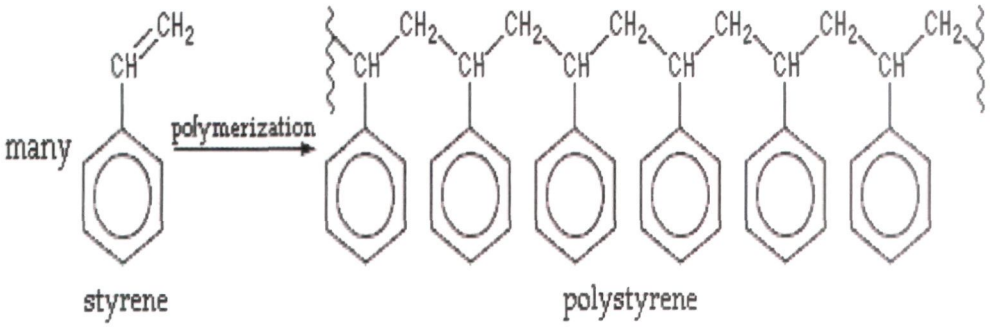

Figure 2 (a). Chemical structure of polystyrene.

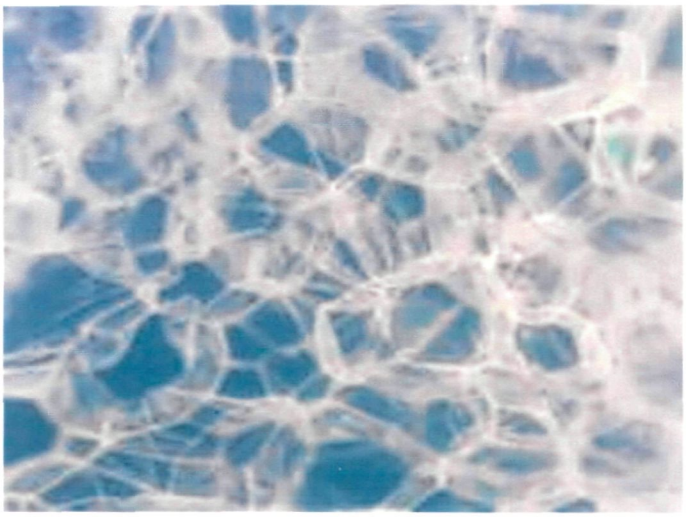

Figure 2 (b). Structure of polystyrene (microscope).

This leads to the formation of an electrical double layer, so that we have a charged surface and a neutralizing excess of counter-ions in the adjacent solution [137,138]. The sign of the membrane charge can be deduced from the chemical structure of the membrane material. In, practice, experiments are required to determine the sign and the density of the membrane charge.

Several applications of charged membranes with fixed-charged density under several conditions include the recovery of high-concentrated acid/alkali fuel cells and high-temperature membrane processes for high efficiency. For these applications, the membranes require the following features: (i) high fixed-charge density and (ii) high thermal, mechanical, and chemical stability. The high fixed-charged density of charged membrane is a useful option. The fixed-charge density of the membrane is estimated by an ionic transport procedure called membrane potential method [139–141]. It has been considered that this phenomenon is attributed to the inhomogeneous fixed-charge distribution or ion-pairing between the fixed-charge groups and counter-ions [142–155]. Mafe *et al.* [151] have proposed a theoretical model considering an ion-pairing effect between fixed-charge groups and counter-ions in charged membranes. According to their paper, most of the fixed-charge groups in the membranes are neutralized by the counter-ions because of the formation of ion-pairs. Chou *et al.* [152–154] studied the ion-pairing effect in an organic solvent system and showed that theoretical predictions of membrane properties, effective charge densities, and ionic mobilities in the membranes agreed well with experimental results from membrane potential and

permeability measurements [155–157]. The membrane potential measurement is a straightforward method for investigating ionic-transport phenomena through charged membranes.

The membrane potential is the potential difference that generated between the electrolyte solutions of different concentrations separated by a charged membrane. Figure 3, shows the membrane transport system used in this study. According to Teorell, Meyer, and Sievers (TMS), the membrane potential in a charged membrane can theoretically be described by the Donnan equilibrium and the Nernst–Planck equation [155–157]. In previous studies, the classical TMS approach was used to analyze experimental membrane potentials in which the charged membrane was treated as having a homogeneous fixed-charge distribution. Charged membranes, however, have an inhomogeneous distribution under the concentration gradient across the membrane, the local concentration of counter-ions in the membrane varied from one surface to the other surface. Mafe *et al.* [149] also suggested a theoretical model to analyze the transport phenomenon across membranes with an inhomogeneous fixed-charge distribution. Here, we tried to expand the conventional theoretical model considering the ion-pairing effect to calculate the potential difference across the membrane with both homogeneous and inhomogeneous fixed-charge distributions. The theoretical model we present here is more versatile for a theoretical analysis of the ionic transport of charged membrane. The objectives of this investigation are as follows: (i) to propose a new ionic-transport model across charged membranes, considering both the effects of an inhomogeneous

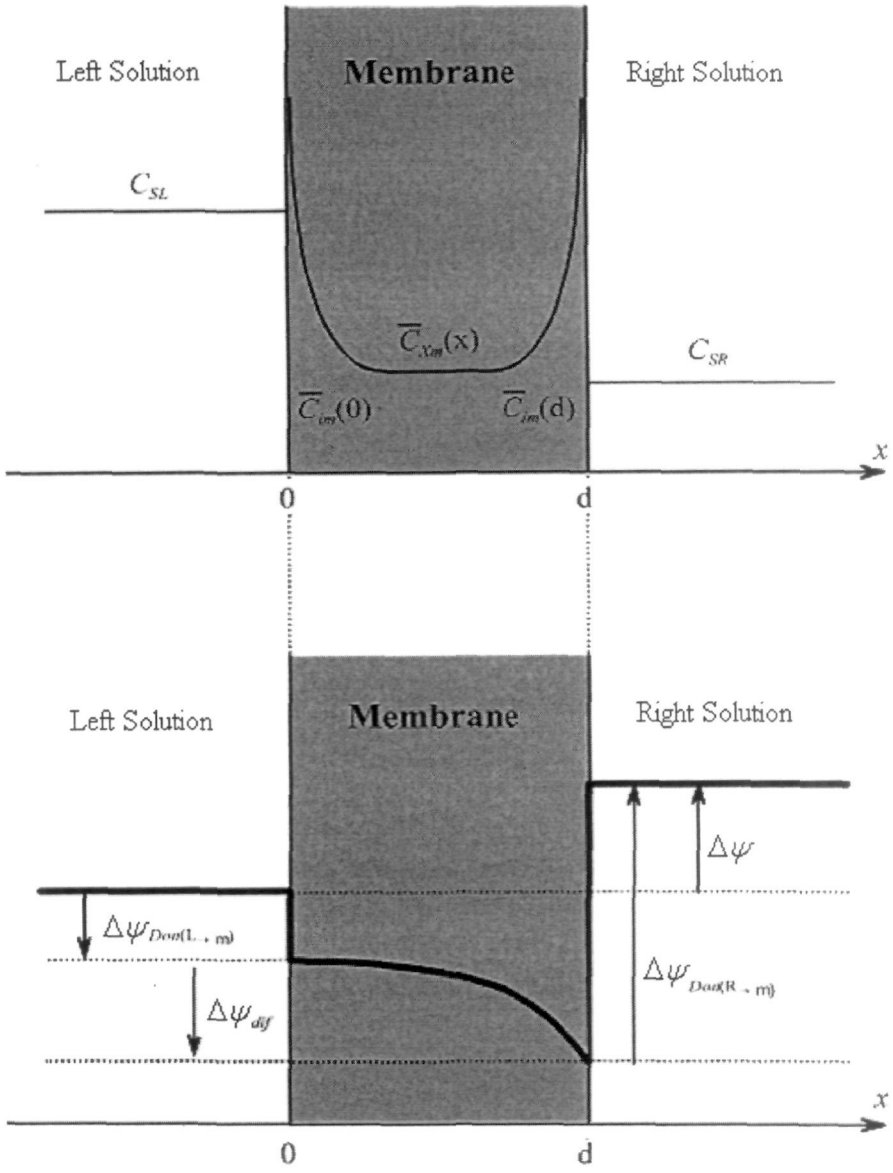

Figure 3. Schematic diagram of the membrane transport system. Ionic concentration profiles (top) and electric potential profiles (bottom) across a charged membrane.

fixed-charge distribution and the ion-pairs in the membrane, and (ii) to estimate theoretically the membrane potentials across charged membranes and the effective charge density of the charged membranes.

1.6 Concept of Ion-Pairs in Membranes

There are many studies on the theories of ion-pairs in electrolyte solutions [158–166]. To estimate the electrostatic interaction between fixed-charge groups and counter-ions in a membrane, we take a very simple model based on the Fuoss approach to ion-pair formation in electrolyte solutions [158]. The fixed-charge groups are paired with the counter-ions [167] in the membrane and is shown in Figure 4. The simplest charged membrane systems interact with three components such as the counter-ions, the co-ions and the fixed-charge groups and these are represented in Figure 4, as $\oplus$, $\ominus$ and $\ominus_{\text{membrane}}$ respectively. When a charged membrane is in contact with an electrolyte solution the counter-ion $\oplus$ opposite charge as the membrane will have a higher concentration in the membrane compared to the solution while the co-ion $\ominus$ have the same charge as the membrane and will have a lower concentration in the membrane. The fixed-charge concentration in the membrane is interacted with counter-ions and form the ion-pairs (neutral molecule) while repel the co-ions because of the same charge as that of the fixed-charged group. The concentration difference of these charged ions generates an electrical potential difference in order to maintain electrochemical equilibrium between the membrane and electrolyte solution [168].

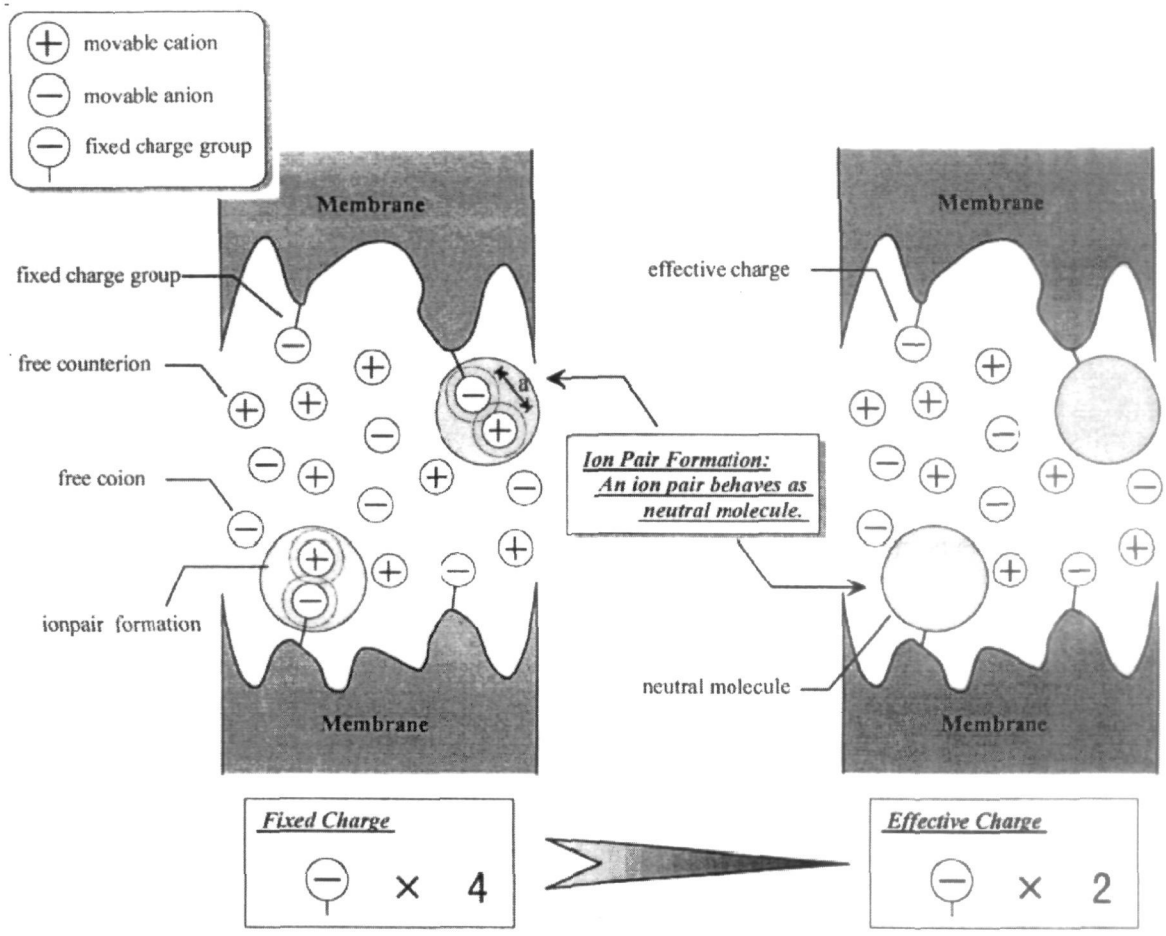

Figure 4. Simplified view of the ion-pair phenomena in a negatively charged membrane.

In order to interpret the variation of the charge effectiveness depending on those values that the ion-pairing effect causes the difference between effective charge. Therefore the fixed-charged groups is represented which is bounded with membrane is shown in Figure 4, and after ion-pair formation i.e., neutralization, the charge group left on the membrane is termed as the effective fixed charged density can be shown in the right side of the Figure 4.

1.7 Characterization of Membrane Morphology

1.7.1 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) was pioneered by Manfred von Ardenne [169,170] and is a type of electron microscope capable of producing high resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample. The SEM is a microscope that uses electrons rather than light to form an image. There are many advantages of using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample

observation makes the SEM one of the most widely used instruments in research areas today [171−178].

Specimen Preparation

There are two basic types of SEM's. The regular SEM, which requires a conductive sample. An environmental SEM can be used to examine a non-conductive sample without coating it with a conductive material. Three requirements for preparing samples for a regular SEM such as:

- Remove all water, solvents, or other materials that could vaporize while in the vacuum.
- Firmly mount all the samples.
- Non-metallic samples, such as bugs, plants, fingernails, and ceramics, should be coated so they are electrically conductive. Metallic samples can be placed directly into the SEM.

Features of Scanning Electron Microscope

SEM is an astonishing instrument for seeing the unnoticed realm of micro-space. Regular light microscopes make use of a series of glass lenses to bend light waves and generate a magnified image. The SEM displays extremely thorough 3-dimensional images at much advanced magnifications than is viable with a light microscope. The images produced without light waves are caused to be black and white. Samples have to be prepared cautiously to endure the vacuum inside the microscope. As the SEM lights them up with electrons, they also have to be prepared to conduct electricity. SEM samples are encrusted with a thin layer of gold by a machine called a sputter coater. The sample is to be found inside the microscope's vacuum column by way of an airtight door.

The spatial resolution of the SEM depends on the size of the electron spot that depends on the magnetic electron-optical system, which produces the scanning beam. The resolution is also restricted by the size of the interaction volume, or the degree to which the material interrelates with the electron beam. The spot size and the interaction volume are both very large in contrast to the distances between atoms, so the resolution of the SEM is not high enough to image down to the atomic scale. The SEM has advantages including the capability to image a comparatively large area of the specimen, the ability to image bulk materials and the diversity of analytical modes accessible for measuring the composition and nature of the specimen.

The following information can be obtained from SEM.

(i) Topography: The surface features of an object or "how it looks", its texture; detectable features limited to a few nanometers

(ii) Morphology: The shape, size and arrangement of the particles making up the object that are lying on the surface of the sample or have been exposed by grinding or chemical etching; detectable features limited to a few nanometers

(iii) Composition: The elements and compounds the sample is composed of and their relative ratios, in areas ~ 1.0 micrometer in diameter

(iv) Crystallographic Information: The arrangement of atoms in the specimen and their degree of order; only useful on single-crystal particles >20 micrometers.

(v) Fracture characterization

(vi) Surface contamination examination

(vii) Failure analysis.

1.7.2 Transmission Electron Microscope (TEM)

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. TEMs use electrons as *light source* and their much lower wavelength makes it possible to get a resolution a thousand times better than with a light microscope. We can see objects to the order of a few angstrom (10^{-10} m) can study small details in the cell or different materials down to near atomic levels. The possibility for high magnification has made the TEM a valuable tool in both medical, biological and materials research. In both cases the specimens must be very thin and able to withstand the high vacuum present inside the instrument.

TEM produces information that complements both neutron and synchrotron X-ray studies. TEM can magnify a sample up to 50 million times its size, with a spatial resolution of 0.1 nanometer (nm). It also has many state-of-the-art attachments that provide powerful tools for researchers to study crystal structure, electronic structure, and chemical composition of materials.

The following information can be obtained from transmission electron microscopy.

Morphology

The size, shape and arrangement of the particles which make up the specimen as well as their relationship to each other on the scale of atomic diameters.

Crystallographic Information

The arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects in areas a few nanometers in diameter.

Compositional Information

The elements and compounds the sample is composed of and their relative ratios, in areas a few nanometers in diameter. There are a number of drawbacks to the TEM technique. Many materials require extensive sample preparation to produce a sample thin enough to be electron transparent, which makes TEM analysis a relatively time consuming process with a low throughput of samples. The structure of the sample may also be changed during the preparation process. Also the field of view is relatively small, raising the possibility that the region analysed may not be characteristic of the whole sample. There is potential that the sample may be damaged by the electron beam, particularly in the case of biological materials.

1.7.3 Atomic Force Microscope (AFM)

The atomic force microscope (AFM) is a very high-resolution type of scanning probe microscope, with demonstrated resolution of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The AFM is one of the foremost tools for imaging, measuring and manipulating matter at the nanoscale. The AFM is being used to solve processing and materials problems in a wide range of technologies affecting the electronics, telecommunications, biological, chemical, automotive, aerospace, and energy

industries. The materials being investigating include thin and thick film coatings, ceramics, composites, glasses, synthetic, biological membranes, metals, polymers, and semiconductors. The AFM is being applied to studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, and polishing. By using AFM one can not only image the surface in atomic resolution but also measure the force at nano-newton scale. The publications [179–185] related to the AFM are growing speedily since its birth.

AFM versus SEM

AFM compared with SEM, AFM provides extraordinary topographic contrast direct height measurements and an unobscured view of surface features, no coating is necessary.

AFM versus TEM

AFM compared with TEM, three dimensional AFM images are obtained without expensive sample preparation and yield far more complete information than the two dimensional profiles available from cross-sectioned samples.

A disadvantage of AFM compared with the SEM is the image size. The SEM can image an area on the order of millimetres by millimetres with a depth of field on the order of millimetres. The AFM can only image a maximum height on the order of micrometres and a maximum scanning area of around 150 by 150 micrometres. Another inconvenience is that at high resolution, the quality of an image is limited by the radius of curvature of the probe tip, and an

incorrect choice of tip for the required resolution can lead to image artifacts. Traditionally the AFM could not scan images as fast as an SEM, requiring several minutes for a typical scan, while an SEM is capable of scanning at near real-time (although at relatively low quality) after the chamber is evacuated. The relatively slow rate of scanning during AFM imaging often leads to thermal drift in the image, making the AFM microscope less suited for measuring accurate distances between artifacts on the image.

In this thesis polystyrene-based titanium phosphate, vanadium phosphate and titanium–vanadium phosphate composite membranes have been prepared using sol–gel method and stability of membranes are described. The membrane–electrolyte system has been considered to contain mainly four chemical species (1) counter-ion (2) co-ion (3) water and (4) the membrane matrix carrying fixed-charged groups. Their behaviors and properties have been examined when these are in contact with various 1:1 electrolyte solutions (KCl, NaCl and LiCl). The surface phenomena and related transport parameters have also been evaluated in order to understand the possible mechanism of ionic-transport through the charged membrane.

The content of the thesis has been separated and presented under the following four heads although certain amount of overlap has been occurred as it is necessary for interpretation and documentation of the content well.

1. General Introduction

2. Preparation and Surface Charge Density of Titanium Phosphate Membranes for Uni-univalent Electrolyte Solution

3. Preparation and Surface Charge Density of Vanadium Phosphate Membranes for Uni-univalent Electrolyte Solution

4. Preparation and Surface Charge Density of $TiPO_4$–VPO_4 Composite Membranes for Uni-univalent Electrolyte Solution

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CHAPTER 2

Preparation and Surface Charge Density of Titanium Phosphate Membranes for Uni-univalent Electrolyte Solution

2.1 Introduction

There has been an increasing interest in the development of new porous solids owing to their wide applications in separation, purification and catalytic processes [1,2]. However, only a few preparative approaches have been reported for the synthesis of mesoporous transition metal phosphates including iron phosphate [3], tin phosphate [4], nickel phosphate [5], zirconium phosphate [6] and titanium phosphates [7,8]. Although most of the mesoporous titanium phosphates have good potential to be used as catalysts for liquid phase oxidation reactions and photo-reactions, no attention has been paid to the study of new sorbents and the ordered porous framework and larger pore size, which can be used in their removal [8]. Thus, inorganic mesoporous materials with a framework of Titanium and zeolitelike ion–exchange properties are highly desirable [9]. Although, there have been many reports on layered and open-framework titanium phosphates. Here, the pore wall of these mesoporous titanium phosphates are composed of Ti, P and O connectivities in which Ti and P have regular alternating tetrahedral arrangements. The unusual ion–exchange properties of these materials are very important to use these materials as it can be adsorbed onto the charged surface of the membrane. The surface of the mesoporous materials are usually hydrophilic in nature containing very large concentrations of defect –OH groups, which can preferentially adsorb water molecules instead of the organic reactant. In order to have good activity, the surface must have to be hydrophobic in nature.

Introducing organic functionalities in the mesoporous pore wall can enhance hydrophobicity of these materials [10,11].

Inorganic precipitate membranes, which are made up of inorganic oxides, will developed an electrical charge due to the amphoteric nature of hydroxyl groups on its surface when it is put in contact with an aqueous medium. To maintain the electro-neutrality of the solution, ions reorganize at the solid-solution interface. The potential varies progressively from the solid surface to the bulk solution in the zone called electrical double layer, composed of a compact and a diffuse layer. Filtration characteristic of the inorganic membranes are affected by electrochemical properties of the solid surface. The electrochemical properties can exert profound influence on the nature and magnitude of the interaction between the membrane and liquid feed, thus affecting permeating fluxes of the solvent and the solute through membrane pores [12,13]. The surface charge properties of membrane materials are among the factors that influence membrane performances and electrical characterizations of the membranes are very important in understanding and predicting filtration properties of the membranes [14–16]. Many inorganic membranes synthesized by a sol–gel process from metal oxides [17–21] have a pore level structure resembling a consolidated or sintered packing of nearly monodisperse, roughly spherical grains [22–24]. It follows that membranes in this subclass of inorganic membranes can be considered as examples of granular porous media with the passages between the grains forming funnel-shaped pores that give rise to a connected porosity [25].

The origin of a membrane charge is obvious and as the membrane brought into contact with an aqueous electrolyte solution, it acquire an electric charge through several possible mechanisms. These mechanisms may include dissociation of functional groups, adsorption of ions from solution, adsorption of polyelectrolytes, ionic surfactants and charged macro molecules. This charging mechanism can take place as well on the exterior membrane surface as on the interior pore surface of the membrane [26,27].

Inorganic membranes show a number of advantageous properties, which make them attractive to filtration tasks in the beverage and textile industry, medicine, pharmacy, chemical industry, waste water treatment and others. These properties are attributed to their high thermal resistance, chemical resistance and mechanical strength. Moreover, inorganic membranes show excellent cleaning conditions, especially by sterilization. Nevertheless, the production costs of inorganic membranes are higher than for membranes made of organic materials because the inorganic membranes are prepared stepwise following traditional inorganic processing steps. The high purity and selectivity of chemicals generally used for synthesizing like these types of membranes are of higher costs; however the processing steps are traditionally inorganic.

In this chapter, we describe the preparation of titanium phosphate membranes using requisite amount of polystyrene as a binder and by applying different pressures. Fixed-charge density, the most effective parameter, has been derived and utilized to calculate membrane potentials for different electrolyte concentrations using TMS equation [28–31] and to test the

applicability of TMS equation for membrane potential for the system under investigation. In addition to the evaluation of surface-charge density, distribution coefficient, transport numbers, mobility, charge effectiveness and other related parameters were calculated for characterizing the prepared membranes.

2.2 Experimental Method

2.2.1 Preparation of membrane

Titanium phosphate precipitate was prepared by mixing a 0.2-mol titanium (III) chloride (Otto Kemi, India with purity of 99.989%) with 0.2-mol tri-sodium phosphate (E. Merck, India with purity of 99.90 %) solutions. The precipitate was washed properly with deionized water (Water purification system, 'Integrate, whose RO conductivity 0–200 μs/cm and UP resistivity 1–18.3 M Ω-cm) to remove free electrolyte and then dried at 80°C. The precipitate was ground into fine powder and was sieved through 200 mesh (granule size < 0.07 mm). Pure crystalline polystyrene (Otto Kemi, India, AR) was also ground and sieved through 200 mesh. The membrane was prepared by the method suggested by Beg *et al.* [32–34]. Appropriate amount of polystyrene and titanium phosphate precipitate were mixed thoroughly using mortar and pestle. The mixture was then kept into a cast die having a diameter of 2.45 cm and placed in an oven (Oven-Universal, Memmert type) maintained at 200°C for about half an hour to equilibrate the reaction mixture. The die containing the mixture was then transferred to a pressure device (SL-89, UK),

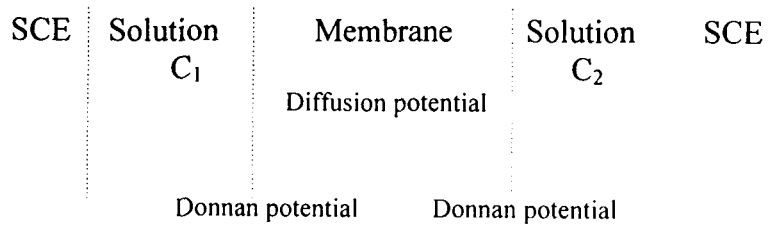
and various pressures such as 80, 100, 120, 140 and 160 MPa were applied during the formation of the membranes. As a result titanium phosphate membrane of approximate thicknesses 0.095, 0.090, 0.085, 0.080 and 0.075 cm were obtained, respectively. Our effort has been to get the membrane of adequate chemical and mechanical stability. The selection and optimum quantity of binder is also of immense important in order to get membranes of adequate mechanical, chemical and thermal stability. Polystyrene is found to be a suitable binder over cellulose acetate, cellulose ester and others for the membrane under investigation. The membranes prepared by embedding 25% of polystyrene were most suitable for our purpose, larger amount and lesser amount of polystyrene did not give reproducible results and appeared to be unstable. The total amount of the mixture thus, utilized for the preparation of the membrane contained 0.125 g of polystyrene and 0.375 g of titanium phosphate. Membranes were fabricated under optimum conditions of temperature and pressure. Membranes prepared in this way were quite stable and did not show any dispersion in water or in other electrolyte solutions. The membranes were subjected to microscopic and electrochemical examinations for cracks and homogeneity of the surface. Only those membranes that had smooth surface and generated reproducible potentials were assured by carefully controlling the conditions of fabrication.

2.2.2 Scanning electron microscopy (SEM)

The samples prepared at various pressures were heated in the tabular furnace for 3 hours and then cooled. A very thin transparent polymer glue tape was applied on the sample. The sample was then placed on an aluminum stub of 15-mm diameter. Thereafter, it was kept in a vacuum chamber at a very low pressure where the entire plastic foil containing the sample was coated with gold (60 μm thickness) for 5 minutes. The scanning electron micrograph of gold coated specimen was recorded, operating at an accelerating voltage of 10 kV using the SEM (JEOL JSM-840).

2.2.3 Measurement of membrane potential

The freshly prepared charged membrane was installed at the center of the measuring cell, which had two glass tubes, one on either side of the membrane. Both collared glass tubes are having a hole for introducing the electrolyte solution and saturated calomel electrodes (SCEs). The half cell contained 25 ml of the electrolyte solutions although the capacity of each of the half cells holding the membrane was about 35 ml. Electrochemical cell of the type and the schematic diagram for the measurement of the membrane potential is shown in Figure 1.



were used for measuring membrane potential [32–34] using Osaw Vernier Potentiometer (Cat.No.30071, UK). In all measurements, the electrolyte

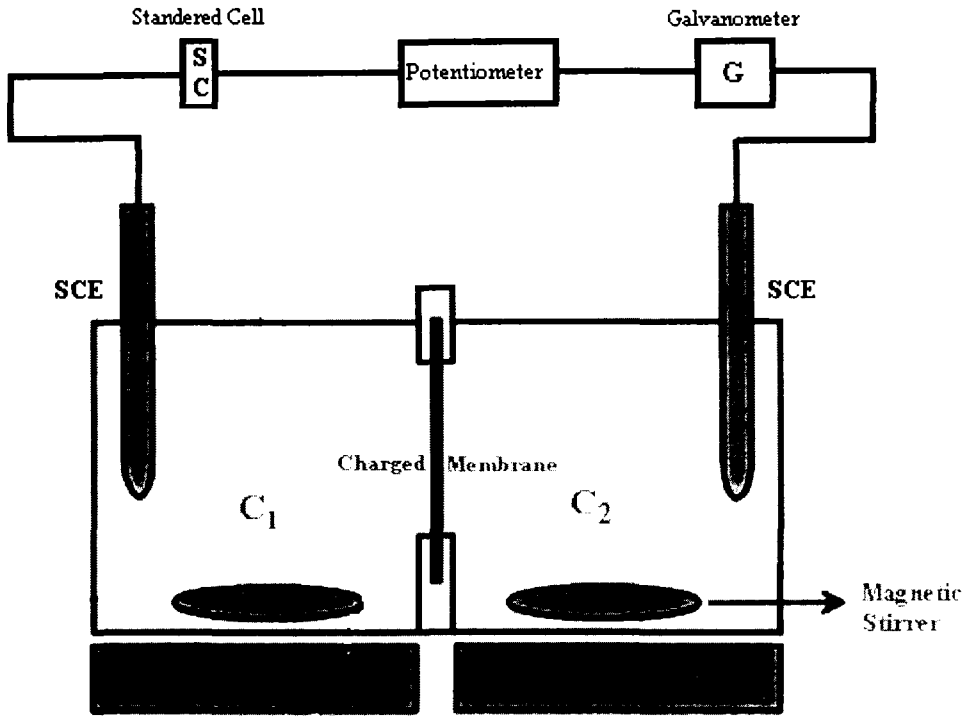


Figure 1. The schematic diagram for the measurement of the membrane potential.

concentration ratio across the membrane was taken as $C_2 / C_1 = 10$. All solutions were prepared by using analytically reagent (AR) grade chemicals and ultra pure distilled water. Saturated calomel electrodes were used and connected to a galvanometer (Osaw, Cat.No.30241, UK). The solutions in both containers were stirred by a magnetic stirrer (Stirrer Cat. No. 2 ML) to minimize the effects of boundary layers on the membrane potential. The pressure and temperature were kept constant throughout the experiment.

2.3 Results and discussion

The titanium phosphate membranes using polystyrene as a binder were prepared by sol–gel process and it was found that these prepared membranes are thermally stable up to 400°C, resistant to compaction, inert to harsh chemical ($K_2Cr_2O_7$, H_2O_2, HNO_3, H_2SO_4 etc.), showing no swelling, stable after long usage and durable. The low cost polystyrene was selected, because its cross-linked rigid framework provides adequate adhesion to the titanium phosphate which accounts for the mechanical stability to the membrane over the other binders like cellulose acetate, cellulose ester etc. Therefore, polystyrene-based titanium phosphate membrane is better than a conventional membrane which degrades under harsh conditions and often encountered in industrial settings. Therefore, it is efficient, cost-effective material having solvent resistance and thermal resistance characteristics [35]. The sintering of inorganic membrane is an important process for tailoring the membrane performance, generally metal based oxides (ZrO_2, TiO_2 Al_2O_3, SiO_2 etc.,) and

their composites modified many of the features like surface morphology, pore radius, porosity and thus affect the membrane performance up to significant extent [36,37]. On sintering the titanium phosphate membrane at 400°C for 6 hours, our results reveled that membrane parameters and surface morphology were almost unchanged as compared to the titanium phosphate membrane at 200°C for about half an hour, it indicates that effect of sintering depend upon the nature of materials.

The characterization of membrane morphology has been studied by a number of investigators using SEM [38,39]. The information obtained from SEM images have provided guidance in the preparation of well ordered precipitates, composite pore structure, micro/macro porosity, homogeneity, thickness, surface texture and crack-free membranes [40,41]. The SEM surface images of the titanium phosphate membranes were taken at different applied pressure and are presented in Figure 2. The SEM images are composed of dense and loose aggregation of small particles and formed pores probably with non-linear channels and are not fully interconnected. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various sizes. The surface openings seem to decrease with increasing applied pressure. The values of membrane potential $\Delta\psi_m$ across the titanium phosphate membranes in contact with various 1:1 electrolyte (KCl, NaCl and LiCl) were dependent on the concentration of electrolyte present on both sides of the membrane at 25±1° C and are given in Table 1. The membrane potential offered by various electrolyte is in the order of LiCl > NaCl > KCl and

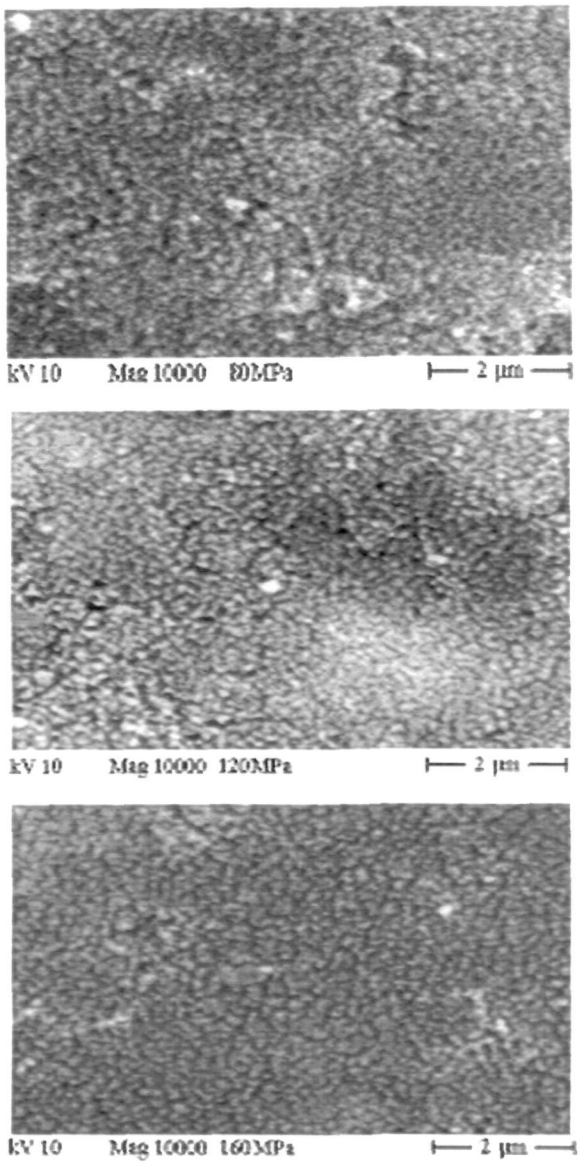


Figure 2. SEM images of polystyrene-based titanium phosphate membranes prepared at different applied pressures of 80, 120 and 160 MPa.

Table 1. The observed, theoretical membrane potentials (mV) and charged density across the titanium phosphate membranes in contact with 1:1 electrolyte solution at different concentrations $C_2/C_1 = 10$ at 25± 1° C.

	Applied Pressure (MPa)														
	80			100			120			140			160		
C_2 (mol/l)	Membrane Potential (O)														
	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl
.0001	53.0	53.8	55.0	54.0	54.5	56.0	55.6	55.9	57.0	56.8	57.0	58.0	57.6	57.8	60.9
.0010	49.2	49.2	50.6	49.8	50.0	51.5	50.6	51.0	52.5	52.0	52.4	53.9	52.5	53.2	55.6
.0100	26.0	26.8	27.0	26.9	27.5	29.0	27.5	28.5	30.0	29.5	29.6	30.9	31.0	3 .6	32.5
.1000	11.0	12.0	12.0	12.0	12.5	14.0	12.5	13.5	15.0	13.5	14.5	16.0	15.0	16.0	17.5
1.000	8.53	9.58	10.0	9.57	10.5	11.0	10.5	11.5	12.2	11.5	12.5	12.5	12.4	14.0	14.9
	Membrane Potential (T)														
.0001	58.94	58.94	58.94	59.01	59.01	59.01	59.12	59.12	59.12	59.14	59.14	59.14	59.16	59.16	59.16
.0010	47.25	47.25	47.26	49.57	49.58	49.58	54.48	54.48	54.48	55.90	55.90	55.90	56.78	56.78	56.78
.0100	11.48	11.50	11.52	13.47	13.48	13.50	20.43	20.44	20.46	24.04	24.05	24.06	27.16	27.17	27.18
.1000	1.364	1.381	1.405	1.595	1.612	1.635	2.516	2.533	2.556	3.090	3.106	3.130	3.661	3.678	3.701
1.000	0.291	0.308	0.319	0.314	0.331	0.342	0.407	0.423	0.435	0.465	0.481	0.493	0.522	0.539	0.550
	Charged Density $\overline{D}$ (eq/l)														
	0.57	0.53	0.34	0.89	0.82	0.40	2.26	2.00	1.49	2.60	2.44	1.69	3.38	2.77	2.23

the decrease in membrane potential with increasing electrolyte concentration is caused by a compression of electrochemical double layers of the membrane surface and in accordance with increasing hydration radii of the electrolyte (LiCl > NaCl > KCl) within the membrane phase [42]. It is accounted for the variation of the membrane potential with the corresponding change in ion concentrations. The observed potential was low (mV, positive) is usual behavior of inorganic membrane and therefore, the titanium phosphate membrane is cation selective and if the value of membrane potential was negative then the membrane become anion selective. This changing pattern of selectivity of the membrane is not peculiar to this system [34]. The selectivity character of ion–exchange membranes with (1:1) and (2:1) or (3:1) electrolyte has been reported by Siddiqi *et al.* [34,43,44] in which the reversal in sign of membrane potential (positive to negative) were occurred with (2:1) and (3:1) electrolyte. This is evidently due to the adsorption of multivalent ions, which led to a state where net positive charge left on the membrane surface made the anion selective with (2:1) or (3:1) electrolyte. On the contrary, 1:1 electrolyte found to be positive value of membrane potential throughout for titanium phosphate membranes. The membrane potential was also seen to be largely dependent on the pressure applied during the membrane fabrication. Application of higher pressure at titanium phosphate membranes led to reduction in their thicknesses, contraction in pore volume and consequently offered a progressively higher fixed charge density [45,46]

which in turn leads to a higher membrane potential can also be analyzed from Table 1.

Inorganic membranes have the ability to generate potential [47,48] when these are used to separate electrolyte solutions. When an ionic gradient is maintained using two solutions of different concentrations of same electrolyte on either side of the membrane, diffusion of electrolyte from the region of higher to lower concentration and flow of water in the opposite direction take place. In fact, the mobile species penetrate the membrane at different magnitude and various transport phenomena, including the development of potential across it, are induced into the system [49]. The fixed-charge group in the membrane matrix greatly influences the counter-ion than co-ion as well as the transport phenomena. The fixed-charge concept of TMS model [29–31] for charged membrane is an appropriate starting point for the investigations of the actual mechanisms of ionic or molecular processes which occur in membrane phase. The TMS model assumes uniform distribution of fixed charge and is not based on structural parameters such as pore radius. This model consists of two Donnan potential and diffusion potential at the two solution membrane interface arising from the unequal concentrations of the mobile ions. According to the TMS equation, the membrane potential $\Delta\overline{\Psi}_m$ is applicable to an idealized system and is given by

$$\Delta\overline{\Psi}_m = 59.2\left(\log\frac{C_2}{C_1}\frac{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}}{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}} + \overline{U}\log\frac{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}\,\overline{U}}{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}\,\overline{U}}\right), \overline{U} = (\overline{u}-\overline{v})/(\overline{u}+\overline{v}) \quad (1)$$

where $\bar{u}$ and $\bar{v}$ are the ionic mobilities of cation and anion ($m^2/V/s$), respectively, in the membrane phase. The charge densities of inorganic membranes were estimated from the membrane potential measurement and can also be estimated from the transport number. To evaluate this parameter for the simple case of a 1:1 electrolyte and a membrane carrying various charge densities $\overline{D} \leq 1$. The theoretical and observed potentials were plotted as a function of $-\log C_2$ as shown by solid and broken lines, respectively in Figure 3 (a, b and c). Thus, the coinciding curve for various electrolyte systems gave the value for the charge density $\overline{D}$ within the membrane phase. The surface charge density $\overline{D}$ of titanium phosphate membranes is found to depend on the applied pressure to which the membrane was subjected to its initial stage of preparation. The width of the titanium phosphate membranes diminished continuously from 0.095–0.075 cm with progressive increase in the applied pressure. The microstructure of dense and loose aggregation of small particles of titanium phosphate membranes which form the interconnected channels and pores appeared to be more compact. The structure is arranged in order, with successive increase in pressure, which can be seen in the SEM in Figure 2. The increase in the values of $\overline{D}$ with higher applied pressure is due to successive increase of charge per unit volume as well as the decrease in pore volume of titanium phosphate membrane and therefore, the degree of selectivity for ions is enhanced with the modification in surface microstructure of membrane (Figure 2).

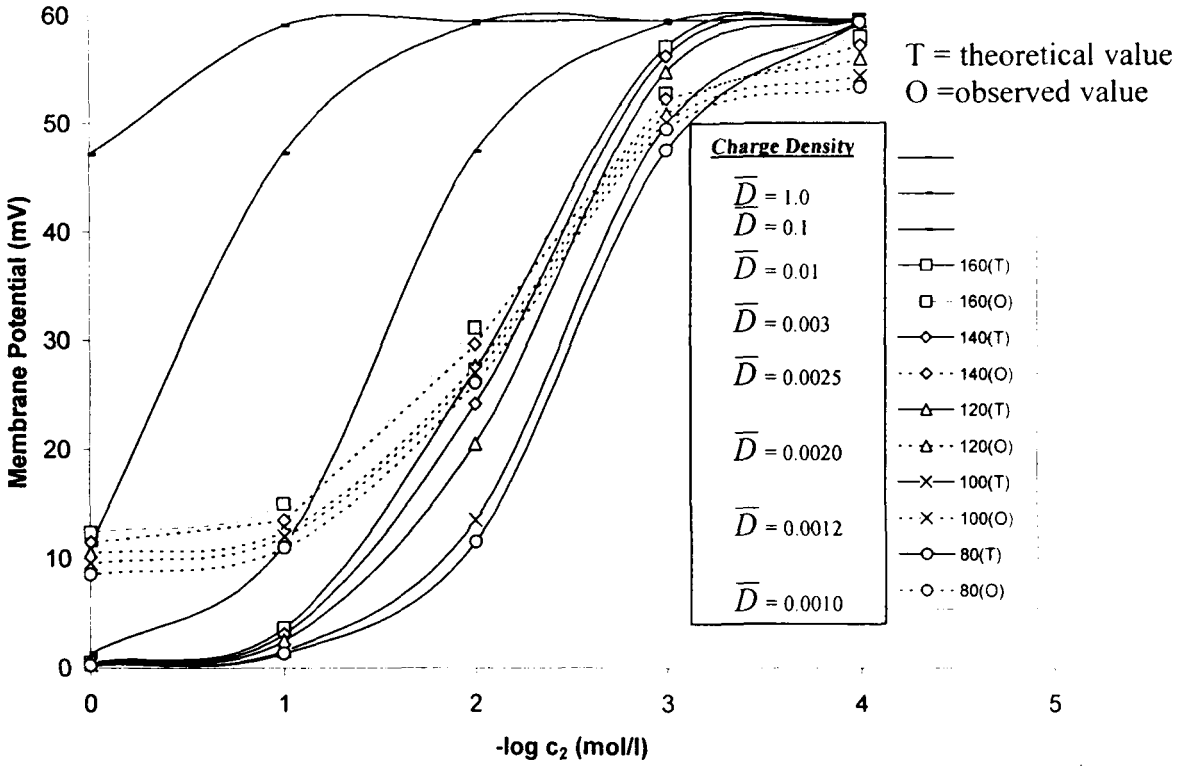


Figure 3 (a). Plots of membranes potential (mV) versus $-\log C_2(\text{mol/l})$ at different concentrations of KCl electrolyte solution for titanium phosphate membranes prepared at different pressures of 80–160 MPa.

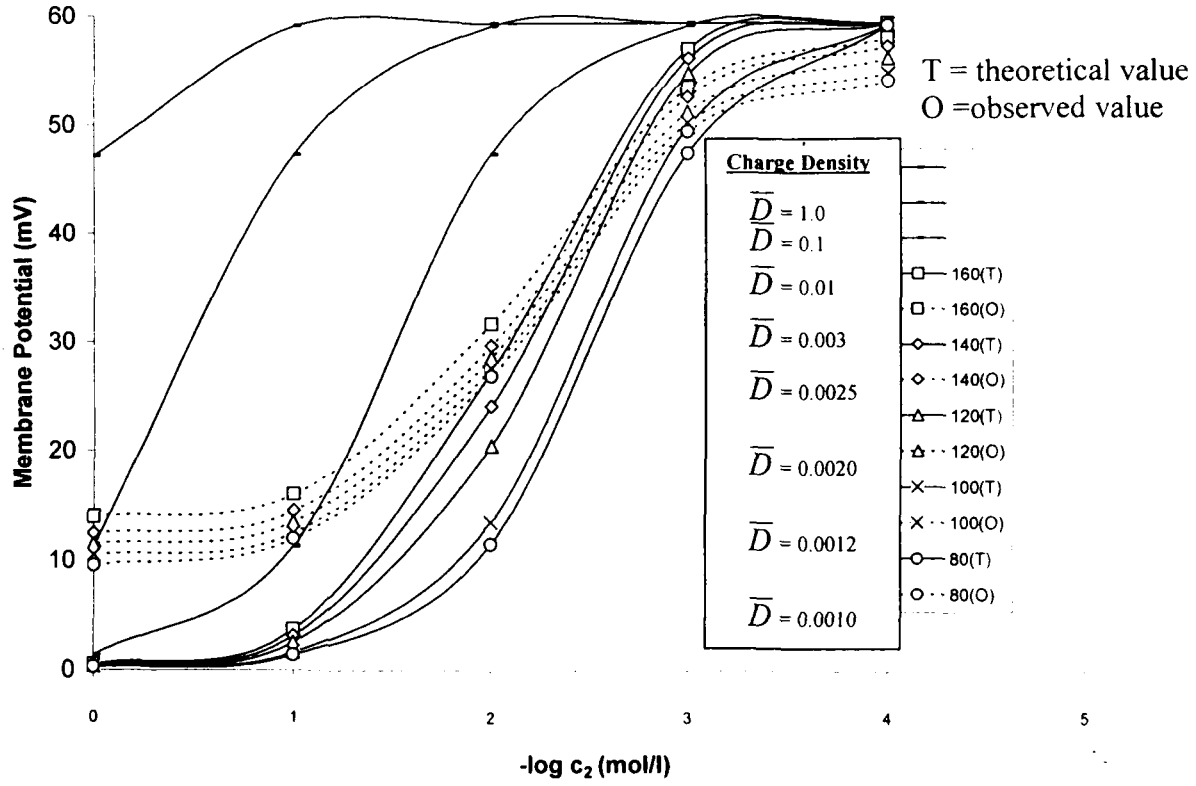


Figure 3(b). Plots of membranes potential (mV) versus $-\log C_2(\text{mol/l})$ at different concentrations of NaCl electrolyte solution for titanium phosphate membranes prepared at different pressures of 80–160 MPa.

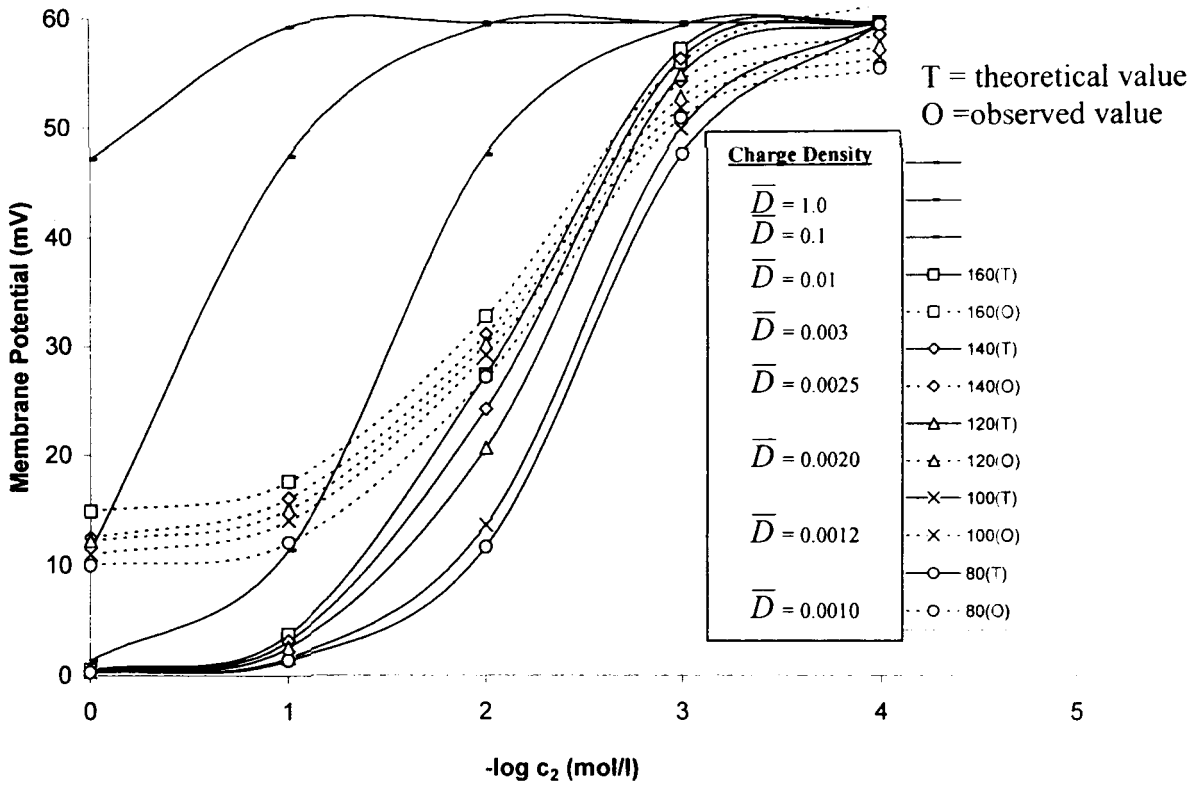


Figure 3(c). Plots of membranes potential (mV) versus $-\log C_2(\text{mol/l})$ at different concentrations of LiCl electrolyte solution for titanium phosphate membranes prepared at different pressures of 80–160 MPa.

The plots of surface charge density $\overline{D}$ of membrane for 1:1 electrolyte (KCl, NaCl and LiCl) versus pressures is shown in the Figure 4 and it is found that the order of charge density for electrolyte used is KCl>NaCl>LiCl. The TMS Equation (1) can also be expressed by the sum of Donnan potential $\Delta\Psi_{Don}$ between membrane surfaces and external solutions and the diffusion potential $\Delta\overline{\Psi}_{diff}$ within the membrane [50,51].

$$\Delta\overline{\Psi}_{m,e} = \Delta\Psi_{Don} + \Delta\overline{\Psi}_{diff} \tag{2}$$

where

$$\Delta\psi_{Don} = -\frac{RT}{V_k F}\ln\left(\frac{\gamma_{2\pm} C_2 \overline{C}_{1+}}{\gamma_{1\pm} C_1 \overline{C}_{2+}}\right) \tag{3}$$

The R, T and F have their usual significance; $\gamma_{1\pm}$ and $\gamma_{2\pm}$ are the mean ionic activity coefficients; $\overline{C}_{1+}$ and $\overline{C}_{2+}$ are the cation concentration in the membrane phase first and second, respectively. The cation concentration is given by the equation

$$\overline{C}_+ = \sqrt{\left(\frac{V_x\overline{D}}{2V_k}\right)^2 + \left(\frac{\gamma_\pm C}{q}\right)^2} - \frac{V_x\overline{D}}{2V_k} \tag{4}$$

where V_k and V_x refer to the valency of cation and fixed-charge group on the membrane matrix, q is the charge effectiveness of the membrane and is defined by the equation

$$q = \sqrt{\frac{\gamma_\pm}{K_\pm}} \tag{5}$$

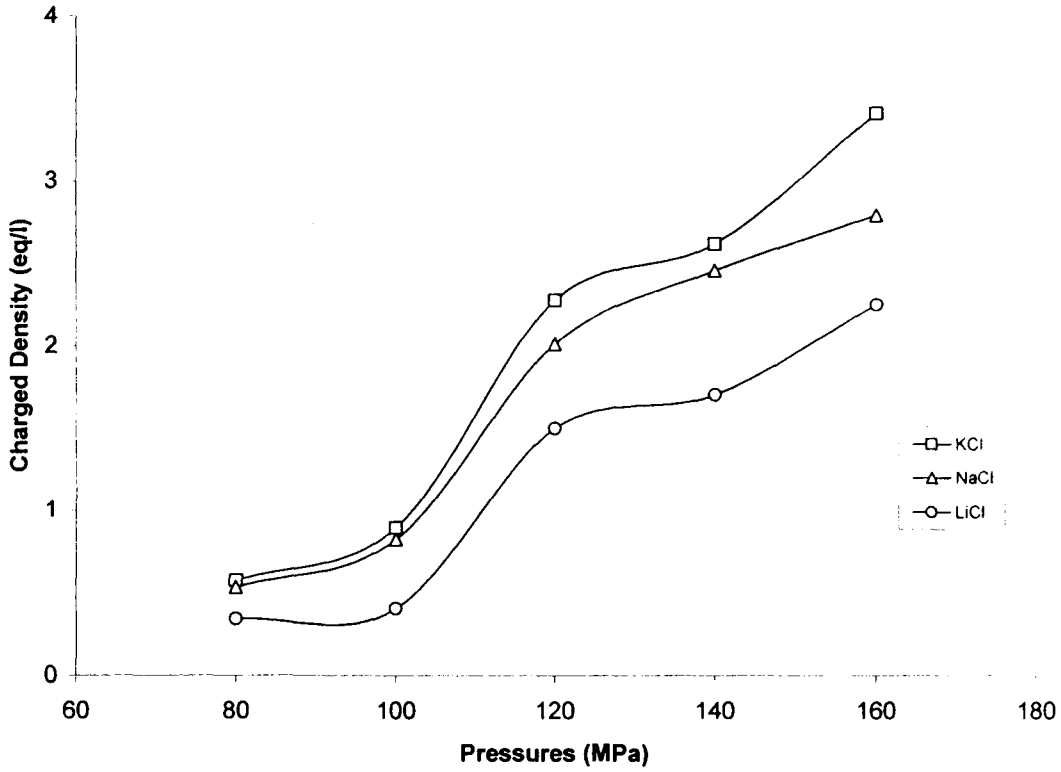


Figure 4. Plots of fixed-charge density $\overline{D}$ (eq/l) versus pressures (80–160 MPa).

where $K_{\pm}$ is the distribution coefficient expressed as;

$$K_{\pm} = \frac{\overline{C}_i}{C_i}, \qquad \overline{C}_i = C_i - \overline{D} \tag{6}$$

where $\overline{C}_i$ is the i^{th} ion concentration in the membrane phase and C_i is the i^{th} ion concentration of the external solution. The transport of electrolyte solutions in pressure-driven membrane has shown that the transport properties of membrane are also controlled by ion distribution coefficients. It appeared that utilizing the Eq. (6) for evaluating the distribution coefficients which were found to have high at lower concentration and as the concentration of electrolyte increases the value of distribution coefficients sharply dropped and thereafter, a stable trend were found and is presented in the Figure 5. The large deviation in $K_{\pm}$ at lower concentration were attributed to the high mobility of comparatively free charges of strong electrolyte and thus reached into the membrane phase easily than that of the higher concentrated electrolyte solution.

The diffusion potential $\Delta\overline{\Psi}_{diff}$, is expressed in the form

$$\Delta\overline{\Psi}_{diff} = -\frac{RT}{V_k F}\frac{\overline{\omega}-1}{\overline{\omega}+1} \times \ln\left(\frac{(\overline{\omega}+1)\overline{C}_{2+} + (V_x/V_k)\overline{D}}{(\overline{\omega}+1)\overline{C}_{1+} + (V_x/V_k)\overline{D}}\right) \tag{7}$$

here $\overline{\omega} = \frac{\overline{u}}{\overline{v}}$ is the mobility ratio of the cation to the anion in the membrane phase. The total membrane potential $\Delta\overline{\Psi}_{m,e}$, was thus obtained by simple addition of Eqs. (3) and (7).

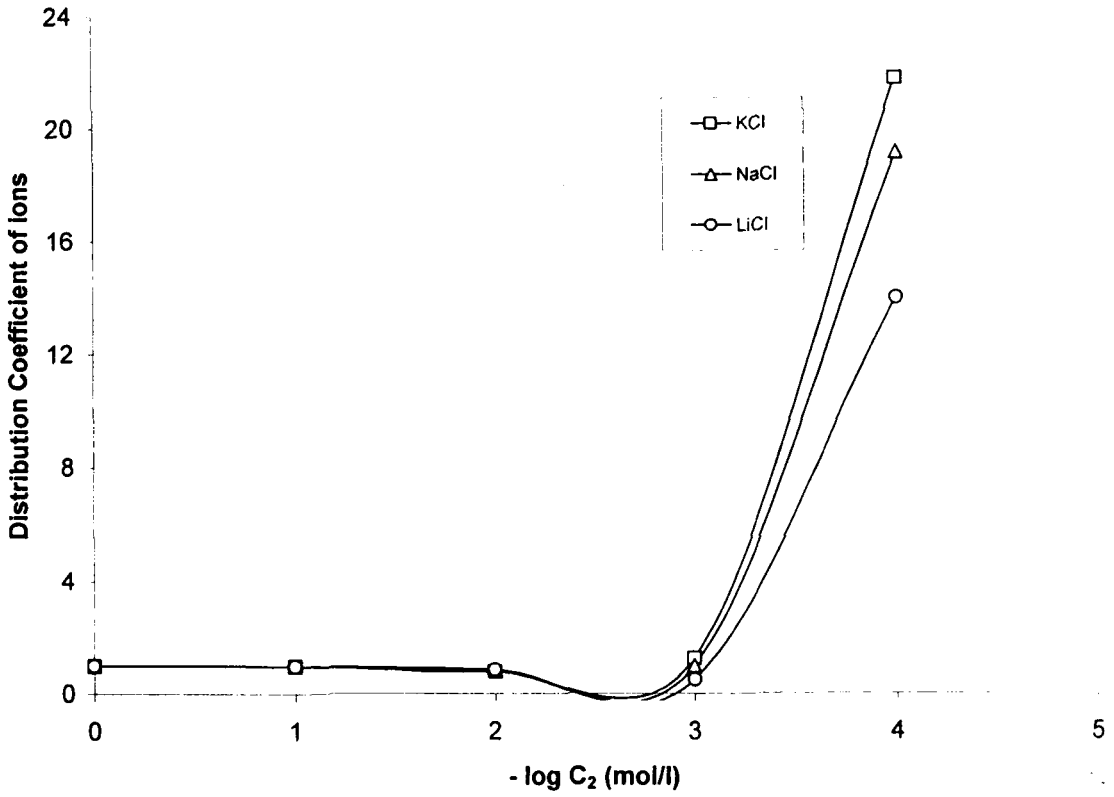


Figure 5. Plots of Distribution coefficient of ions ($K_{\pm}$) versus $-\log C_2(\text{mol/l})$.

$$\Delta\overline{\psi}_{m,e} = -\frac{RT}{V_k F}\ln\left(\frac{\gamma_{2\pm}C_2\overline{C}_{1+}}{\gamma_{1\pm}C_1\overline{C}_{2+}}\right) - \frac{RT}{V_k F}\frac{\overline{\omega}-1}{\overline{\omega}+1}\times\ln\left(\frac{(\overline{\omega}+1)\overline{C}_{2+}+(V_x/V_k)\overline{D}}{(\overline{\omega}+1)\overline{C}_{1+}+(V_x/V_k)\overline{D}}\right) \quad (8)$$

In order to test the applicability of these theoretical equations for the system under investigation, the Donnan potential and diffusion potential were separately calculated from the membrane parameters obtained from membrane potential measurements using a typical membrane prepared at a pressure of 120 MPa.

$$\Delta\overline{\psi}_m = \frac{RT}{F}(t_+ - t_-)\ln\frac{C_2}{C_1} \quad (9)$$

$$\frac{\overline{u}}{\overline{v}} = \frac{t_+}{t_-} \quad (10)$$

Equation (9) and (10) were first used to get the values of transport numbers t_+ and t_- from experimental membrane potential data and consequently, the mobility ratio $\overline{\omega} = \frac{\overline{u}}{\overline{v}}$ and $\overline{U}$ were calculated and given in Table 2. The mobility $\overline{\omega}$ of the electrolyte in the membrane phase were found to be high at lower concentration with the electrolyte used (KCl, NaCl and LiCl) and followed by a sharp drop in the values were resulted on further increasing the concentration, is given in the Table 2. The high mobility is attributed to higher transport number of comparatively free cations of electrolyte which was also found to be the similar trend as the mobility in least concentrated solution.

Donnan and diffusion potential at various electrolyte concentrations can be calculated from the parameters $\gamma_{1\pm}$, $\gamma_{2\pm}$, $\overline{C}_{1+}$, $\overline{C}_{2+}$, $\overline{\omega}$, V_x, V_k and the

Table 2. The values of t_+, $\overline{U}$, $\overline{\omega}$ and $K_\pm$, q, $\overline{C}_+$ evaluated using Eq. (9) and Eqs. (4)–(6) respectively, from observed membrane potentials for various electrolyte at different concentrations for titanium phosphate membranes prepared at 120 MPa pressure.

C_2(mol/l)	t_+	$\overline{U}$	$\overline{\omega}$	$K_\pm$	q	$\overline{C}_+$
KCl (Electrolyte)						
.0001	0.96	0.92	24.0	21.60	0.215	0.00001
.0010	0.92	0.84	11.5	1.260	0.875	0.00013
.0100	0.73	0.46	2.70	0.774	1.078	0.00555
.1000	0.60	0.20	1.50	0.977	0.887	0.08326
1.000	0.59	0.18	1.40	0.997	0.779	0.77445
NaCl						
.0001	0.97	0.94	32.3	19.00	0.229	0.00003
.0010	0.93	0.86	13.3	1.000	0.982	0.00015
.0100	0.74	0.48	2.85	0.800	1.062	0.00602
.1000	0.61	0.22	1.56	0.980	0.890	0.08447
1.000	0.60	0.20	1.50	0.998	0.810	0.80688
LiCl						
.0001	0.98	0.96	49.0	13.90	0.268	0.00008
.0010	0.94	0.88	15.7	0.490	1.404	0.00014
.0100	0.75	0.50	3.00	0.851	1.030	0.00676
.1000	0.63	0.26	1.70	0.985	0.895	0.08600
1.000	0.61	0.22	1.56	0.998	0.880	0.87724

experimentally derived values of charge density $\overline{D}$ by using Eqs. (3) and (7). The values of the parameters $K_{\pm}$, q and $\overline{C}_{+}$ derived for the system have also been given in Table 2. The values of $\gamma_{\pm}$ were the usual charted values for electrolyte (KCl, NaCl and LiCl). The membrane potential derived in this way and the experimentally obtained membrane potentials at different concentrations for various electrolyte systems have been compared and provided in Figure 6. It may be noted that the experimental data follow the theoretical curve quite well. However, some deviations may be due to various non ideal effects, such as swelling effect and osmotic effects. These effects are often simultaneously present in the charged membranes.

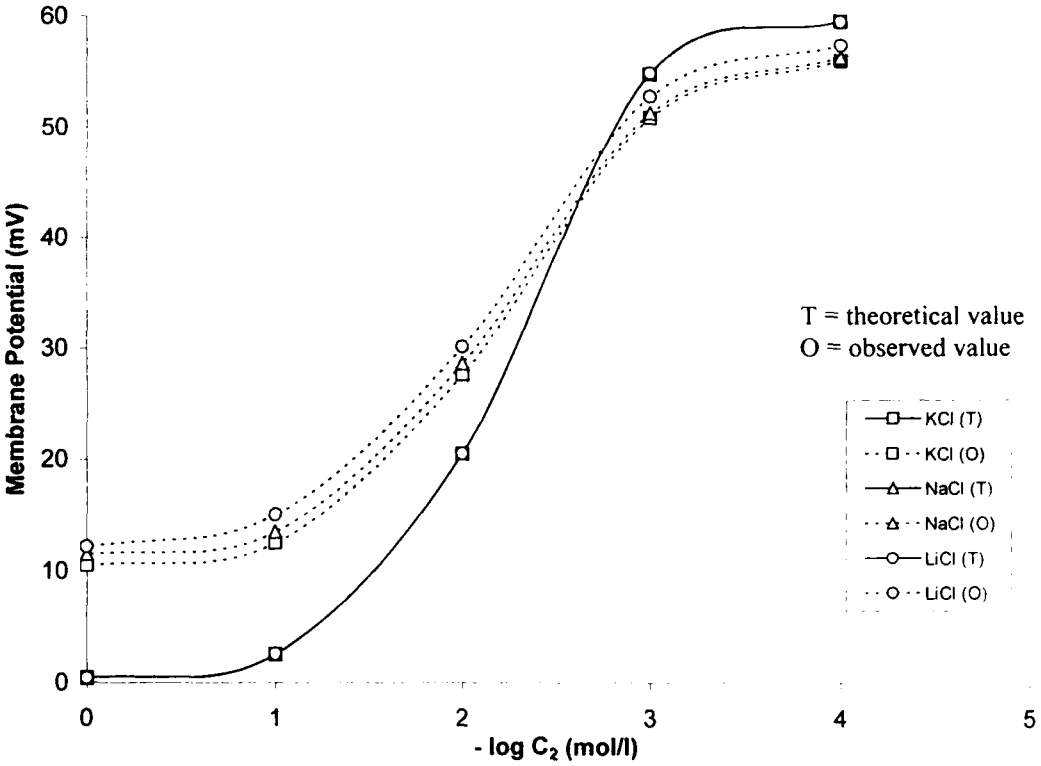


Figure 6. Membranes potential across titanium phosphate membranes using various electrolyte (1:1) solutions at different concentrations.

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CHAPTER 3

Preparation and Surface Charge Density of Vanadium Phosphate Membranes for Uni-univalent Electrolyte Solution

3.1 Introduction

Vanadium phosphate constitutes a very interesting class of layered compound which exist in a wide range of structural forms both due to the variable valency of vanadium as well as the large diversity in the bonding of the VO_6 octahedron and the PO_4 structural units [1]. Several phases containing vanadium in +5, +4 and +3 oxidation states are known. In all these compounds the layers are held together by hydrogen bonding or by weak Van der Waal's interactions. There are different approaches that have been adopted to synthesise novel phases in the VPO system as well as modify the structures of some known analytically important vanadium phosphate phases. Some of these new and modified phases have been investigated and it has been observed that when metal ions are incorporated into the VPO phase during its preparation in organic medium, the basic structure of the parent compound is retained [2]. One of the major areas of research in the quest for new materials is the synthesis of new open structures with pores in the mesoporous range as well as lamellar phases of mesoscopic dimensions [3–5]. Since, it is encouraging to study on the aspect of surface charge density and related parameters of materials like vanadium phosphate as a composite membrane.

The application of extraction techniques for removal and recovery of metals is very significant nowadays. Increasing demand of metal production led to the research of more efficient and economical methods of purification required by industry. Membrane technology has become an important alternative to the processes employed for wastewater (electroplating, mining

etc.) treatments, separation and recovery of target metals. Selective transport of metal ions has been widely studied with supported liquid membranes [6,7]. A membrane is said to be ideally ion–selective if only either positively or negatively charged ions pass through it. On the other hand if migration of ions through a membrane is not affected at all, the membrane is said to be non-selective. Most often the membranes are neither ideally ion–selective nor entirely non-selective in nature; they exhibit ion–selectivity in some extent depending on the nature of the membrane forming materials, its dimensional and electrochemical characteristics. Membrane potential studies are commonly used for the electrochemical characterization of membranes [8,9]. Their high selectivity, high diffusion rates and the possibility of concentrating ions make them particularly useful. Despite the well-known advantages of supported liquid membranes, they are not often used for practical separation processes because of their low stability and high degradation rate. These membranes suffer the loss of carrier by dissolution into the aqueous phases and many different studies have been performed to stabilize them [10–12]. Some researchers have impregnated the membranes with low molecular weight strong acids (e.g. phosphoric acid, sulfuric acid, and $CFSO_3H$) [13,14]. The conductivity of acid doped membranes can be as twice high as that of Nafion [14]. Unfortunately these low molecular weight acids are leached out of the membranes over tens to hundreds of hours. Increased mechanical strength and decreased swelling has been achieved by crosslinking the polymer chains in the membrane. The addition of resin in the composite membrane increases the

ion–exchange capacity, decreases the extent of swelling with water absorption and increases the mechanical strength.

Inorganic filtration membranes show a number of advantageous properties, which make them attractive to filtration processes in the beverage and textile industry, medicine, pharmacy, chemical industry and waste water treatment. These properties are attributed to their high thermal resistance, chemical resistance and mechanical strength. Inorganic membranes are prepared stepwise following traditional inorganic processing steps [15] and show excellent cleaning conditions, especially by sterilization.

In this chapter, we describe the preparation of vanadium phosphate membrane by sol–gel process using polystyrene as a binder by applying different pressures. The surface charge density is the most important parameter controlling the membrane phenomena that have been derived and used to calculate the membrane potential for different electrolyte concentrations using Teorell, Meyer and Sievers (TMS) method [16–19] and to test the applicability of TMS equation for membrane potential for the system under investigation. In addition to the evaluation of surface charge density, distribution coefficient, transport numbers, mobility, charge effectiveness and other related parameters were calculated for characterizing the prepared membranes.

3.2 Experimental Method

3.2.1 Preparation of membrane

Vanadium phosphate precipitate was prepared by mixing a 0.2-mol vanadium (III) chloride (Merck, Germany with 99.989% purity) with 0.2-mol tri-sodium phosphate (E. Merck, India with 99.90% purity) solutions. The precipitate was properly washed with deionized water (Water purification system, 'Integrate, whose RO conductivity 0–200 μs/cm and UP resistivity 1–18.3 M Ω-cm) to remove free electrolyte and dried at 80°C. The precipitate was ground into fine powder and was sieved through 200 mesh (granule size < 0.07 mm). Pure crystalline polystyrene (Otto Kemi, India, AR) was also ground and sieved through 200 mesh. The membrane was prepared by the method suggested by Beg *et al.* [20–22]. Appropriate amount of polystyrene and vanadium phosphate precipitate were mixed thoroughly using mortar and pestle. The mixture was then kept into a cast die having diameter of 2.45 cm and placed in an oven (Oven-Universal, Memmert Type) maintained at 200°C for about half an hour to equilibrate the reaction mixture. The die containing the mixture was then transferred to a pressure device (SL-89, UK) and various pressures such as 80, 100, 120, 140 and 160 MPa were applied during the membrane formation. As a result vanadium phosphate membrane of approximate thicknesses 0.095, 0.090, 0.085, 0.080 and 0.075 cm were obtained, respectively. Our effort has been to get the membrane of adequate chemical, thermal and mechanical stability. The membranes prepared by embedding 25% of polystyrene were most suitable for our purpose, larger amount (> 25%) and lesser amount (< 5%) of polystyrene did not give reproducible results and appeared to be unstable. The total amount of the

mixture thus, utilized for the preparation of the membrane contained 0.125 g of polystyrene and 0.375 g of vanadium phosphate. Membranes were fabricated under optimum conditions of temperature and pressure. Membranes prepared in this way were quite stable and did not show any dispersion in water or in other electrolyte solutions. The membranes were subjected to microscopic and electrochemical examinations for cracks and homogeneity of the surface and only those which had smooth surface and generated reproducible potentials were assured by carefully controlling the conditions of fabrication.

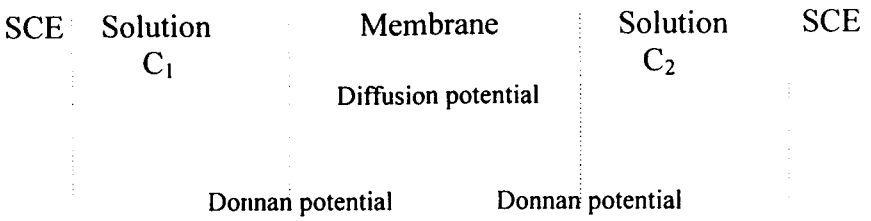
3.2.2 Scanning electron microscopy (SEM)

The prepared samples at various pressures were heated in the tabular furnace for 3 hours and then cooled. A very thin transparent polymer glue tape was applied on the sample and then placed on an aluminum stub of 15-mm diameter. Thereafter, the sample was kept in a chamber at a very low pressure where the entire plastic foil containing the sample was coated with gold (60 μm thickness) for 5 minutes. The scanning electron micrograph of gold coated specimen was recorded, operating at an accelerating voltage of 10 kV using the Scanning electron microscope (JEOL JSM-840).

3.2.3 Measurement of membrane potential

The freshly prepared charged membrane was installed at the center of the measuring cell, which had two glass containers, one on either side of the membrane. Both collared glass containers are having a hole for introducing the electrolyte solution and saturated calomel electrodes (SCEs). The half cell

contained 25 ml of the electrolyte solution while the capacity of each of the half cells holding the membrane was about 35 ml. Electrochemical cells of the type



were used for measuring membrane potential [20–22] using Osaw Vernier Potentiometer (UK). In all measurements, the electrolyte concentration ratio across the membrane was taken as $C_2 / C_1 = 10$. All solutions were prepared by using analytical reagent (AR) grade chemicals and ultra pure distilled water. The electrodes used were saturated calomel electrode and were connected to a galvanometer (Osaw, Spot reflecting galvanometer, UK). The solutions in both containers were stirred by a magnetic stirrer (Cat. No.2 ML, Remi-Equipments) to minimize the effects of boundary layers on the membrane potential. The pressure and temperature were kept constant throughout the experiment and the potentials were measured at 25°C.

3.3 Results and discussion

The characterization of membrane morphology has been studied by a number of investigators using Scanning electron microscopy (SEM) [23,24]. The information obtained from SEM images have provided guidance in the preparation of well ordered precipitate, composite pore structure, micro/macro porosity, homogeneity, thicknesses, surface texture and crack-free membrane

[25,26]. The SEM surface images of the vanadium phosphate membranes were taken at different applied pressure and are presented in Figure 1. The SEM images are composed of dense and loose aggregation of small particles and formed pores probably with non-linear channels and are not fully interconnected. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various sizes. The surface openings seem to decrease with increasing applied pressure. Inorganic membranes have the ability to generate potential [27,28] when two solutions of unequal concentration of electrolyte are separated by a membrane, the solute and solvent are driven by the differences in their chemical potential acting across the membrane. The electrical character of the membrane regulates migration of charge species for the membrane, diffusion of electrolyte from the region of higher to lower concentration and flow of water in the opposite direction take place [29]. The values of observed membrane potential $\Delta\psi_m$, measured across polystyrene-based vanadium phosphate membranes in contact with various 1:1 electrolyte at 25±1°C are given in Table 1. The values of membrane potential across the membranes with 1:1 electrolyte (KCl, NaCl and LiCl) were found dependent on the concentration of electrolyte present on the both sides of the membrane.

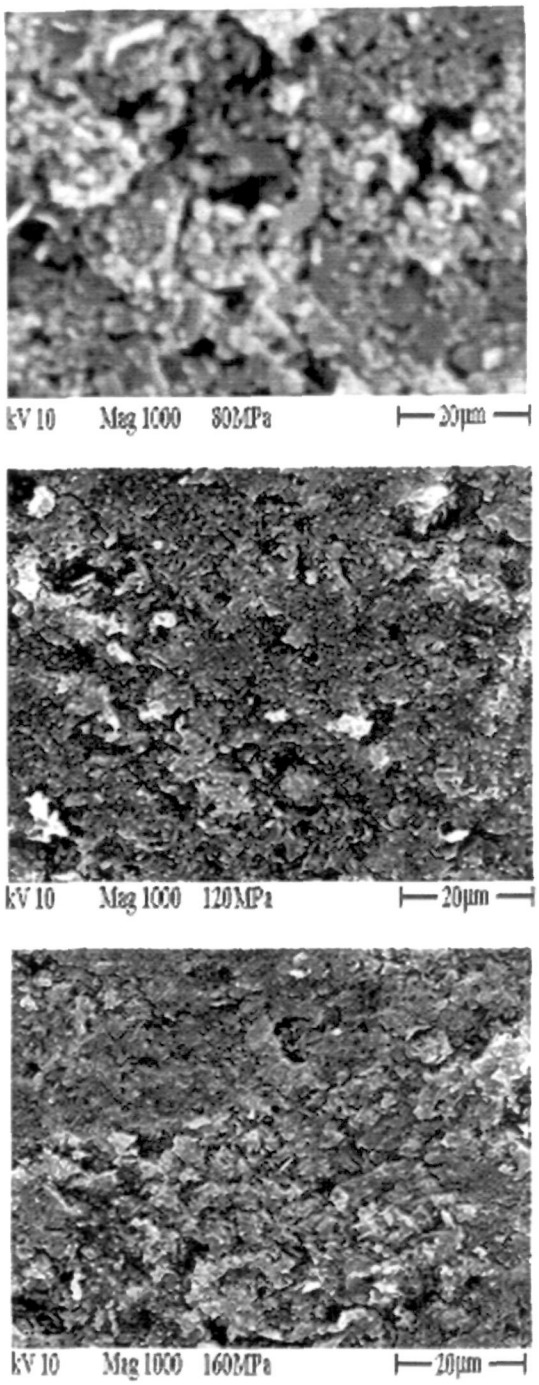


Figure 1. SEM images of polystyrene-based vanadium phosphate membranes prepared at different applied pressures of 80, 120 and 160 MPa.

Table 1. Observed, theoretical membrane potentials (mV) and charge density across the vanadium phosphate membranes in contact with 1:1 electrolyte solution at different concentrations $C_2/C_1 = 10$ at 25±1° C.

	Applied Pressure (MPa)														
	80			**100**			**120**			**140**			**160**		
C_2 (mol/l)	**Membrane Potential (O)**														
	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl
.0001	48.3	49.0	49.9	50.2	51.0	52.2	51.0	51.8	52.9	52.0	53.2	54.7	53.4	54.5	55.6
.0010	43.3	44.0	45.3	45.2	46.0	47.0	46.2	47.3	48.2	47.3	48.5	50.0	48.2	49.3	50.5
.0100	20.8	21.8	23.0	23.0	23.9	24.8	24.2	25.3	26.2	25.2	25.9	27.0	26.0	26.8	27.9
.1000	6.30	7.00	7.96	8.00	8.72	10.0	9.30	10.0	11.1	10.0	10.8	12.6	11.0	12.6	13.3
1.000	4.00	4.63	5.90	5.20	6.08	7.58	7.02	7.59	8.59	7.53	8.50	9.75	8.50	9.50	10.5
	Membrane Potential (T)														
.0001	58.94	58.94	58.94	59.01	59.01	59.01	59.12	59.12	59.12	59.14	59.14	59.14	59.16	59.16	59.16
.0010	47.24	47.24	47.25	49.57	49.57	49.57	54.48	54.48	54.48	55.90	55.90	55.90	56.78	56.78	56.78
.0100	11.44	11.45	11.47	13.42	13.41	13.45	20.39	20.40	20.41	24.00	24.01	24.02	27.13	27.14	27.15
.1000	1.310	1.322	1.340	1.541	1.553	1.571	2.462	2.474	2.492	3.036	3.048	3.066	3.608	3.620	3.638
1.000	0.232	0.242	0.258	0.255	0.265	0.281	0.348	0.357	0.374	0.406	0.415	0.432	0.463	0.473	0.490
	Charged Density $\overline{D}$ (eq/l)														
	1.98	1.73	1.39	2.07	1.79	1.53	4.86	3.95	3.32	7.56	6.29	4.63	13.6	10.3	7.83

The potential was low at higher concentrations which is usual behavior of inorganic membrane. All the values of membrane potential across the membranes were found to be positive when it was used to separate various solutions of the electrolyte (1:1) and therefore, the membrane is cation selective and if the value of membrane potential was negative (which is not found in our observation) then the membrane become anion selective. This changing pattern of selectivity of the membrane is not peculiar to this system [22]. The selectivity character of ion–exchange membranes with (1:1) and (2:1) or (3:1) electrolyte is already reported [22,30,31] in which the reversal in sign (positive to negative) of membrane potential values were occurred is evidently due to the adsorption of multivalent ions, which led to a state where net positive charge left on the membrane surface making anion selective with (2:1) or (3:1) electrolyte. The simplest charged membrane systems interact with four components such as, the solvent water, the counter-ions, the co-ions and the fixed-charges. Our systems carry charge of 0, -1, +1 and +3 respectively. When a charged membrane is in contact with an electrolyte solution the counter-ion is Cl^-, which is an opposite charge to the membrane will have a higher concentration in the membrane compared to the solution while the co-ions, Li^+, Na^+ and K^+ have the same charge as the membrane and will have a lower concentration in the membrane. The fixed- charge concentration in the membrane is due to vanadium (III), which interacts with hydrated counter-ion and form the ion-pairs by loosing much of the water content while repelling the co-ions because of the same charge as that of the fixed- charged group. The

concentration difference of these charged ions generates an electrical potential difference in order to maintain electrochemical equilibrium between the membrane and electrolyte solution [32].

The membrane potential was also seen to be largely dependent on the pressure applied during the membrane formation. The vanadium phosphate membranes prepared at successive higher applied pressure gave progressively high potential, reduced thicknesses and pore volume whereas raised mechanical transport resistance and the surface charge density [33,34] which in turn modified other features of membrane. The membrane is macroscopically uniform in thickness and is porous in nature. The pores are modeled as uniform capillaries that extend throughout the membrane. These pores are evenly distributed throughout the surface of the membrane (cross-section). Entrance and exit effects are ignored since the membrane thickness is large compared to the pore radius. As the compactness of the membranes is increased with increasing the applied pressure the dispersity of the charge distribution on membrane is modified. However, the thickness is still large compared to the pore radius and it is assumed that the membrane and adjacent solution (interfaces) are in equilibrium. The distribution of charge density and mobile species within the pores are assumed to be uniform [35]. Since, the surface charge model work as tool to improve the performance of the membrane filtration process and charge property of the membrane matrix greatly influences the counter-ion than co-ion as well as the transport phenomena in the solution. The surface charge concept of TMS model [16–18] for charged

membrane is an appropriate starting point for the investigations of the actual mechanisms of ionic or molecular processes which occur in membrane phase. The TMS model assumes uniform distribution of surface charge and consists of two Donnan potential and diffusion potential at the two solution membrane interface arising from the unequal concentrations of the mobile ions. The membrane potential $\Delta\overline{\Psi}_m$, according to TMS model and applicable to an idealized system is given by

$$\Delta\overline{\Psi}_m = 59.2\left(\log\frac{C_2}{C_1}\frac{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}}{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}} + \overline{U}\log\frac{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}\,\overline{U}}{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}\,\overline{U}}\right),\quad \overline{U} = (\overline{u}-\overline{v})/(\overline{u}+\overline{v}) \tag{1}$$

where $\overline{u}$ and $\overline{v}$ are the ionic mobilities of cation and anion ($m^2/V/s$), respectively, in the membrane phase. The charge densities of inorganic membranes were estimated from the membrane potential measurement and can also be estimated from the transport number. To evaluate this parameter for the simple case of a 1:1 electrolyte and a membrane carrying various charge densities $\overline{D} \leq 1$. The theoretical and observed potentials were plotted as a function of $-\log C_2$ and shown by solid and broken lines, respectively in Figure 2 (a, b and c). Thus, the coinciding curve for various electrolyte systems gave the value for the charge density $\overline{D}$ within the membrane phase. The surface charge density $\overline{D}$ of vanadium phosphate membranes were found to depend on the applied pressure to which the membrane was subjected to its initial stage of the preparation.

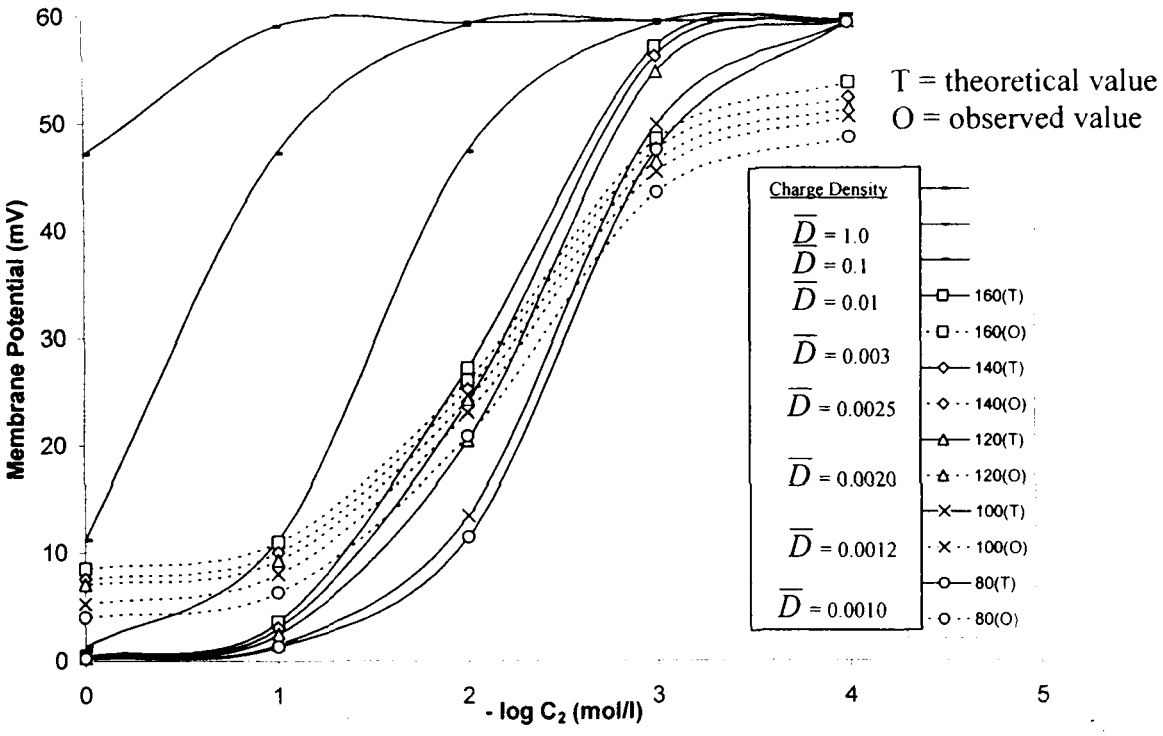


Figure 2 (a). Plots of membranes potential (mV) versus $-\log C_2\,(\mathrm{mol/l})$ at different concentrations of KCl electrolyte solution for vanadium phosphate membranes prepared at different pressures of 80–160 MPa.

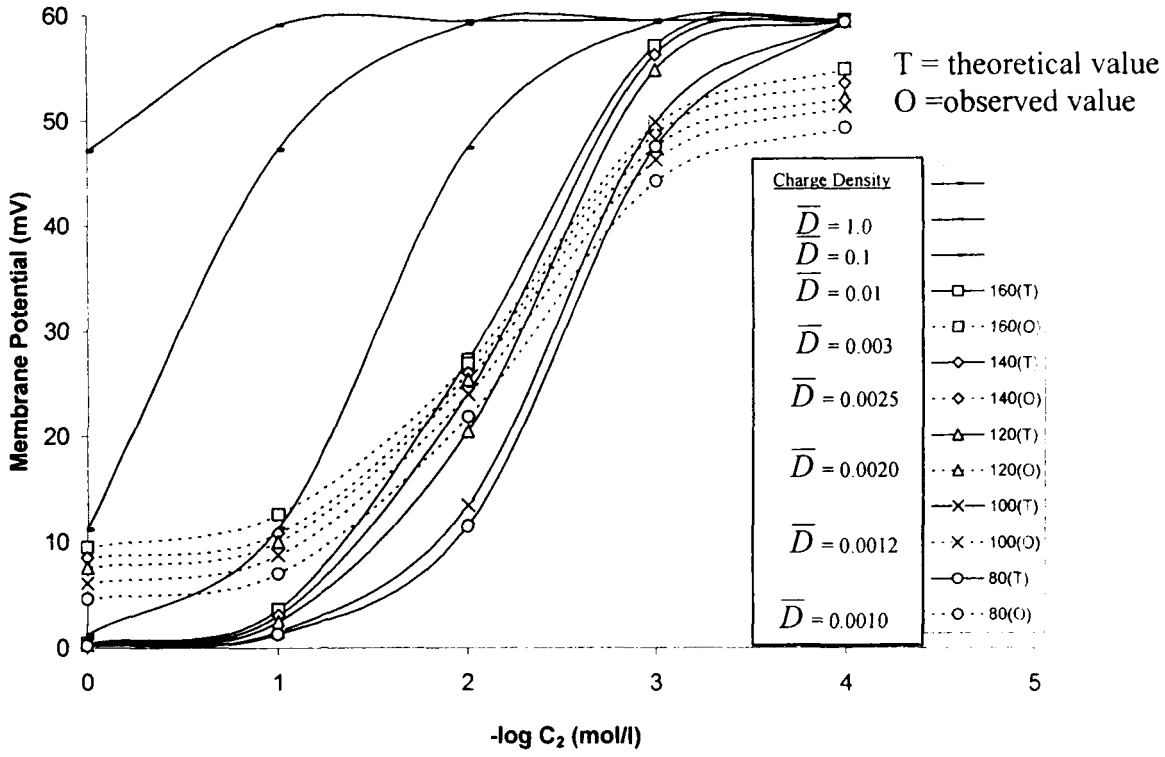


Figure 2 (b). Plots of membranes potential (mV) versus $-\log C_2\,(\mathrm{mol/l})$ at different concentrations of NaCl electrolyte solution for vanadium phosphate membranes prepared at different pressures of 80–160 MPa.

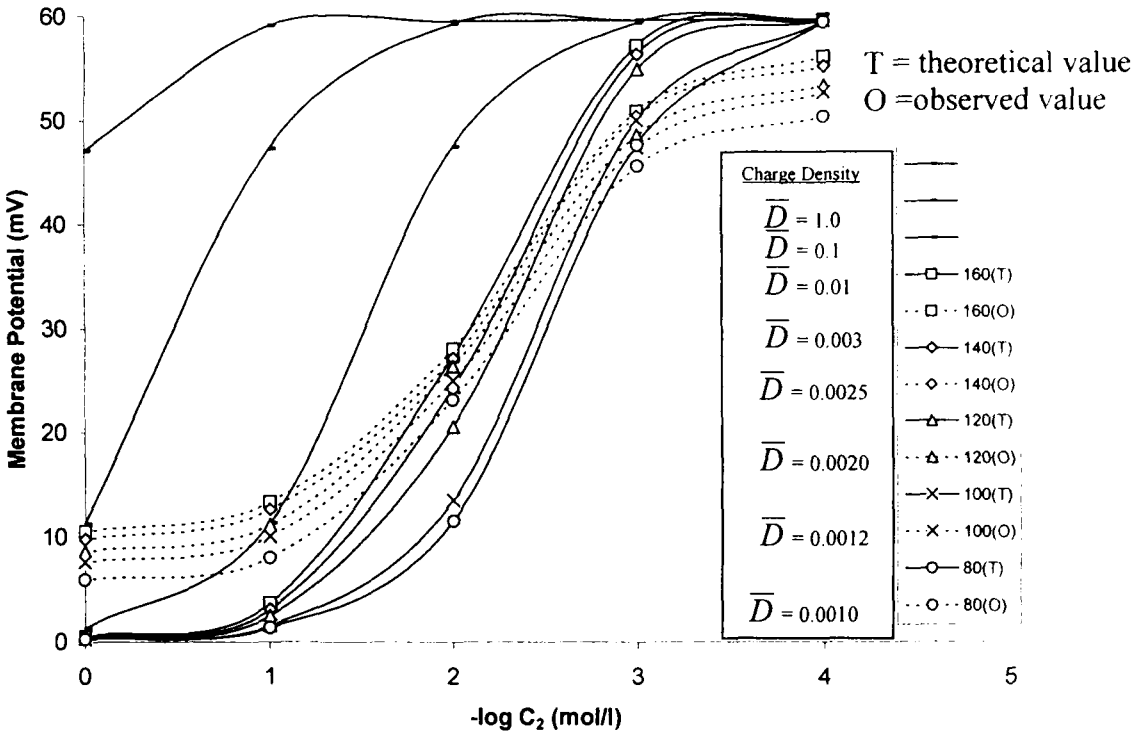


Figure 2 (c). Plots of membranes potential (mV) versus $-\log C_2 (\mathrm{mol/l})$ at different concentrations of LiCl electrolyte solution for vanadium phosphate membranes prepared at different pressures of 80–160 MPa.

The successive increases in applied pressure on vanadium phosphate membranes reduced the width d, from 0.095–0.075 cm. The microstructure of dense and loose aggregation of small particles which form the interconnected channels and pores appeared to be more compact and arranged in order with progressive increase in pressure can also be seen in the SEM (Figure 1). Therefore, increase in the values of $\overline{D}$ with increased applied pressure is due to the increase in charge per unit volume of the membranes. It is pertinent to note that the applied pressure is related to the thickness as well as the surface charge density $\overline{D}$ of the membrane within a studied range. In Figure 3, the applied pressure and their corresponding thicknesses of the membranes were taken at the abscissa and the surface charge density $\overline{D}$ at an ordinate for 1:1 electrolyte (KCl, NaCl and LiCl). From these plots, it clearly indicate that with the increasing pressure, increase in the compactness (reduced in width) is observed which lead to decrease in pore size of the membrane as a result increase in the solution flux and corresponding increase in the surface charged density of the membrane were appeared for given electrolyte solutions. Membrane performance is significantly modified by permeants of electrolyte solutions; rejection generally increases with increasing pressure (solution flux) as well as the reduction in thickness of membranes. However, when rejection reaches a minimum the contribution of increasing water flux becomes important, thus rejection increases with increasing pressure or reduction in thickness of membranes [36].

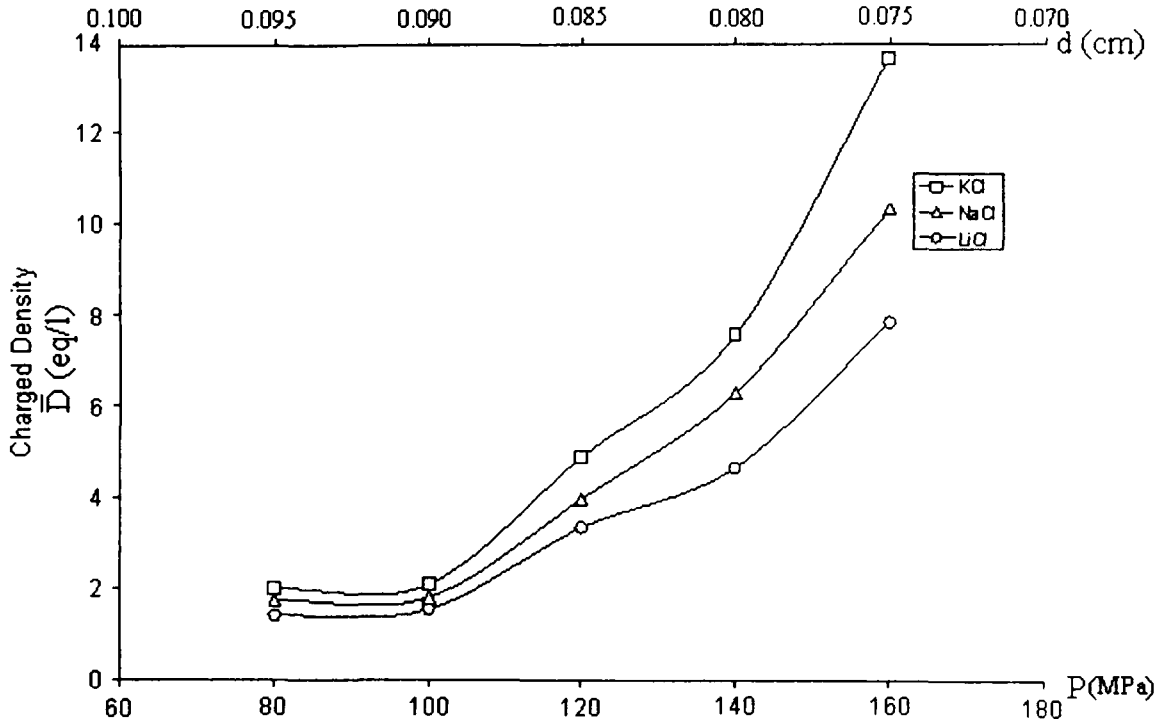


Figure 3. Plots of fixed-charge density (eq/l) $\overline{D}$ versus pressures (80–160 MPa).

Therefore, the orders of rejection of permeants are according to the surface charge density of the membranes for the electrolyte KCl>NaCl>LiCl.

The TMS equation (1) can also be expressed by the sum of Donnan potential $\Delta\Psi_{Don}$, between the membrane surfaces and the external solutions, and the diffusion potential $\Delta\overline{\Psi}_{diff}$, within the membrane [37,38].

$$\Delta\overline{\Psi}_m = \Delta\Psi_{Don} + \Delta\overline{\Psi}_{diff} \tag{2}$$

$$= -\frac{RT}{V_k F}\ln\left(\frac{\gamma_{2\pm}C_2\overline{C}_{1+}}{\gamma_{1\pm}C_1\overline{C}_{2+}}\right) - \frac{RT}{V_k F}\frac{\overline{\omega}-1}{\overline{\omega}+1}\times\ln\left(\frac{(\overline{\omega}+1)\overline{C}_{2+}+(V_x/V_k)\overline{D}}{(\overline{\omega}+1)\overline{C}_{1+}+(V_x/V_k)\overline{D}}\right) \tag{3}$$

The R, T and F have their usual significance; $\gamma_{1\pm}$ and $\gamma_{2\pm}$ are the mean ionic activity coefficients; $\overline{\omega} = \frac{\overline{u}}{\overline{v}}$ is the mobility ratio of the cation to anion in the membrane phase whereas the $\overline{C}_{1+}$ and $\overline{C}_{2+}$ are the cation concentration in the membrane phase first and second, respectively, and is given by the equation

$$\overline{C}_+ = \sqrt{\left(\frac{V_x\overline{D}}{2V_k}\right)^2 + \left(\frac{\gamma_\pm C}{q}\right)^2} - \frac{V_x\overline{D}}{2V_k} \tag{4}$$

where V_k and V_x refer the valency of cation and fixed-charge group on the membrane matrix, q is the charge effectiveness of the membrane and is defined by the equation

$$q = \sqrt{\frac{\gamma_\pm}{K_\pm}} \tag{5}$$

where $K_{\pm}$ is the distribution coefficient expressed as

$$K_{\pm} = \frac{\overline{C}_i}{C_i}, \qquad \overline{C}_i = C_i - \overline{D} \tag{6}$$

where $\overline{C}_i$ is the i^{th} ion concentration in the membrane phase and C_i is the i^{th} ion concentration of the external solution. The transport of electrolyte solutions in pressure-driven membrane has shown that the transport properties of membrane are also controlled by ion distribution coefficients. It appeared that utilizing the equation (6) for evaluating the distribution coefficients which were found to be high at lower concentration and as the concentration of electrolyte increases the value of distribution coefficients, sharply dropped and thereafter, a stable trend was found and is presented in Table 2. The large deviation in distribution coefficients ($K_{\pm}$) at lower concentration were attributed to the high mobility of comparatively free charges of strong electrolyte and thus reached into the membrane phase easily than that of the higher concentrated electrolyte solution.

In order to test the applicability of these theoretical equations for the system under investigation, the Donnan potential and diffusion potential were separately calculated from the membrane parameters obtained from membrane potential measurements using a typical membrane prepared at a pressure of 120 MPa.

$$\Delta\overline{\psi}_m = \frac{RT}{F}(t_+ - t_-)\ln\frac{C_2}{C_1}, \qquad \frac{t_+}{t_-} = \frac{\overline{u}}{\overline{v}} \tag{7}$$

Table 2. The values of t_+, $\overline{U}$, $\overline{\omega}$ and $K_\pm$, q, $\overline{C}_+$ evaluated using Eq. (9) and Eqs. (4) – (6) respectively, from observed membrane potentials for various electrolyte at different concentrations for vanadium phosphate membranes prepared at 120 MPa pressure.

KCl (Electrolyte)						
C_2(mol/l)	t_+	$\overline{U}$	$\overline{\omega}$	$K_\pm$	q	$\overline{C}_+$
.0001	0.92	0.84	11.5	47.60	0.144	0.00003
.0010	0.88	0.76	7.33	3.860	0.500	0.00024
.0100	0.70	0.40	2.33	0.514	1.323	0.00267
.1000	0.57	0.14	1.33	0.951	0.899	0.07855
1.000	0.55	0.10	1.22	0.995	0.780	0.76966
NaCl						
.0001	0.93	0.86	13.3	38.50	0.161	0.00005
.0010	0.89	0.78	8.09	2.950	0.572	0.00025
.0100	0.71	0.42	2.45	0.605	1.221	0.00357
.1000	0.58	0.16	1.38	0.960	0.900	0.08074
1.000	0.56	0.12	1.27	0.996	0.811	0.80299
LiCl						
.0001	0.94	0.88	15.7	32.20	0.176	0.00002
.0010	0.90	0.80	9.00	2.320	0.645	0.00021
.0100	0.72	0.44	2.57	0.668	1.163	0.00425
.1000	0.59	0.18	1.44	0.966	0.904	0.08255
1.000	0.57	0.14	1.33	0.996	0.881	0.87358

Equation (7) was first used to get the values of transport numbers t_+ and t_- from experimental membrane potential data and consequently, the mobility ratio $\overline{\omega} = \frac{\overline{u}}{\overline{v}}$ and $\overline{U}$ were calculated and given in Table 2. The mobility $\overline{\omega}$ of the electrolyte in the membrane phase were found to be high and the order is LiCl>NaCl>KCl. When, the external electrolyte concentration is higher or lower, a number of counter-ions go into the membrane due to the imbalance in the counter-ion concentration of external electrolyte and fixed-charged group in the membrane phase. Therefore, the ion association with the fixed-charged group and counter-ions in the membrane is enhanced as a result the charge effectiveness and has a lower value whereas in the moderate concentration region the counter-ion concentration in the external electrolyte and the fixed-charge density in the membrane are comparable [39–41]. Therefore, a less number of ion-pair formation and consequently higher values of the charged effectiveness, the optimum value of charge effectiveness are obtained at around C_2 = 0.01 mol/l and then decreased steeply as shown in Figure 4. The order of the charge effectiveness of 1:1 the solute-solute interaction and ionic radii of the counter-ions. According to structural hydration interaction (SHI) [42] model which is based on the effect to account for many thermodynamic properties of small solutes in water. It seems to be the effect of hydration on the solute-solute interaction electrolyte may depend on increasing ionic charge density of co-ion adsorption on the charged membranes.

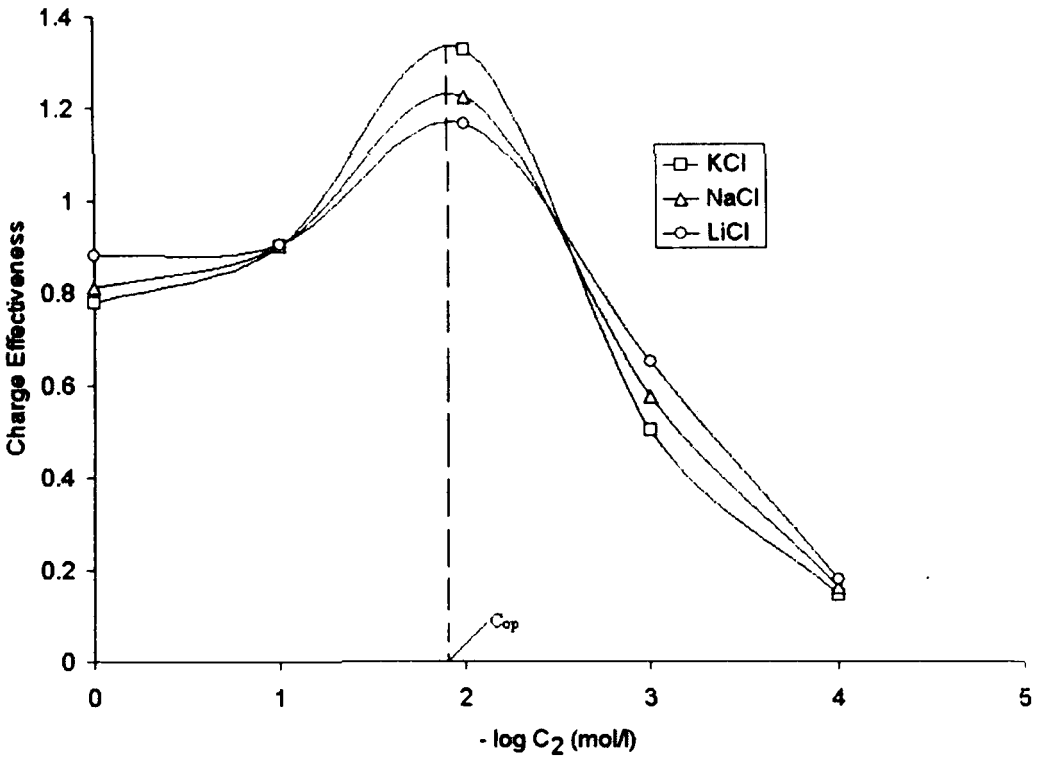


Figure 4. Plots of Charge effectiveness versus -log C_2 (mol/l) for 1:1 electrolyte at different concentrations.

The charge effectiveness depends upon the hydration of with the fixed-charge group is overcome on the electrostatic interaction between the fixed-charge group and the counter-ion. Therefore, the charge effectiveness q, values is increased as the hydration radii of the electrolyte (KCl<NaCl<LiCl).

The membrane potentials derived in this way (theoretical) and the experimentally obtained membrane potentials at different concentrations for various electrolyte systems have been compared and provided in Figure 5. It may be noted that the experimental data follow the theoretical curve quite well. However, some deviations may be due to various non ideal effects; such as swelling effect and osmotic effects. From Figure 6, the plots are describe the deviation of potential ($\Delta\Psi_d$) from the theoretical values (ideal) versus –log C_2. Since, these deviations are due to various non ideal effects such as swelling and osmotic effects which are prominent and simultaneously present in the membrane [38]. A ratio of the swelling effect/osmotic effect can also be explained by deviation from theoretical potential values of the membrane. The swelling effect is dominating over the osmotic effect at higher concentration region and resulting in negative deviation from the ideality while at lower concentration osmotic effect is overcome over the swelling effect due to the excess of solvent molecules and found to be a positive deviation from the ideal values [32]. In between the two extreme concentrations, the ratio of the swelling effect/osmotic effect approaches to 1 but reverses in sign and reaches to the optimum concentration $C_{op,}$ at which the deviation in potential

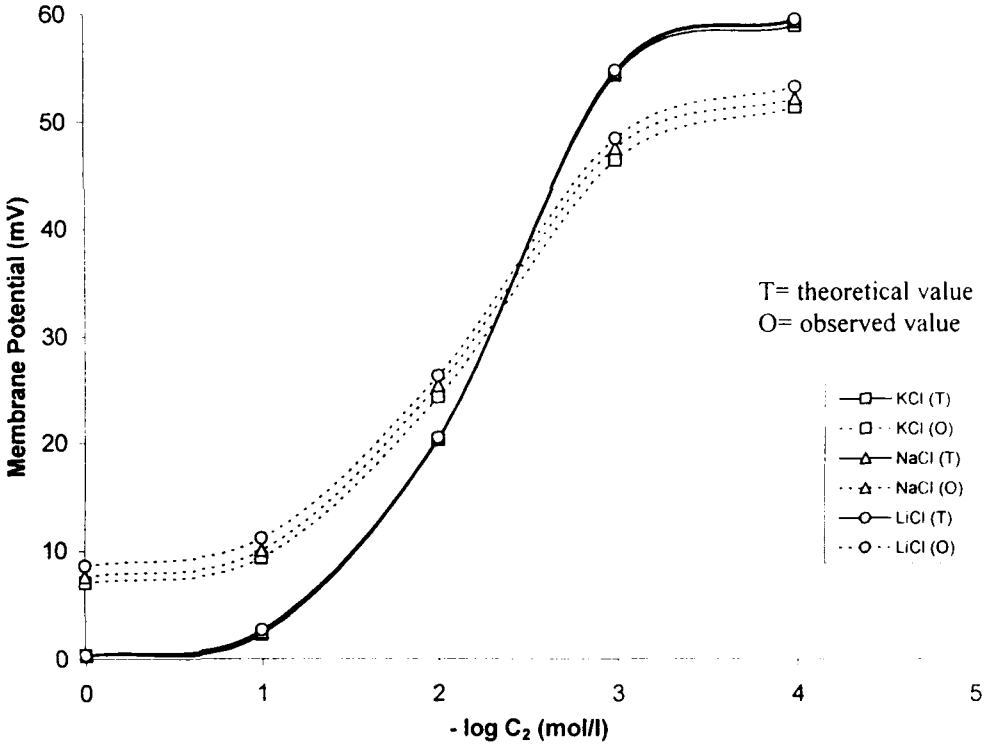


Figure 5. Membranes potential across vanadium phosphate membranes using various electrolyte (1:1) solutions at different concentrations.

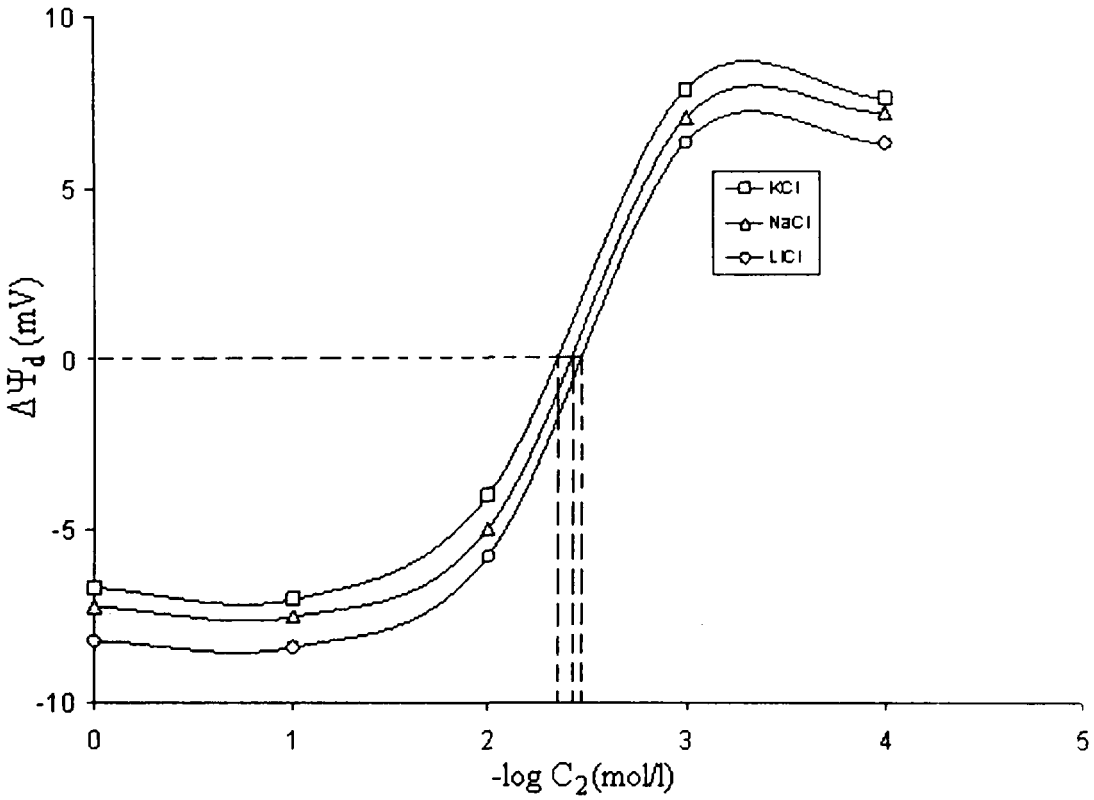


Figure 6. Plots for the deviation in membrane potential $\Delta\psi_d$ (mV) versus $-\log C_2$ (mol/l).

approaches zero or theoretical potential coincide with the observed potential for various (1:1) electrolyte. The optimum concentration C_{op} for various (1:1) electrolyte is found to be in the concentration range of 0.01– 0.001 mol/l.

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CHAPTER 4

Preparation and Surface Charge Density of $TiPO_4$–VPO_4 Composite Membranes for Uni-univalent Electrolyte Solution

4.1 Introduction

The inorganic materials with a framework of titanium and zeolite-like ion–exchange properties are highly desirable. Although, there have been many reports on layered and open framework [1] of titanium phosphates, vanadium phosphates constitute a very interesting class of layered compounds, which exist in a wide range of structural forms both due to the variable valency of vanadium as well as the large diversity in the bonding of the VO_6 octahedron and the PO_4 structural units [2]. Phosphate-based molecular sieves [3] have attracted widespread attention of the academia and industry because of their interesting 2-D and 3-D framework topologies. The cation–exchange materials are very common among inorganic materials (e.g. zeolites), whereas anion–exchange inorganic materials are very rare [4]. A great technological interest has developed among scientists in polymer composites because improvements in properties can be done by reinforcing it with additional materials. In doing so it is ensured that overall properties of the composites are superior to those of the individual components. Moreover, mass production of these composites is efficient and economical [5]. Composite membranes have high thermal and chemical stability, long life and good defouling properties in their applications and they can have catalytic properties [6]. These properties have made these membranes desirable for industrial applications in the food, pharmaceutical and electronic industries. The potential application of composite membranes at elevated temperatures requires more study and further improvement in the composite membrane preparation. The sol–gel approach is

considered to be the most practical one for composite membrane synthesis [7]. Apart from the conventional ceramic technique, there are various techniques like coating, evaporation, CVD and sputtering [8]. The sol–gel technique is used to prepare a porous ceramic membrane [9] because it allows for high-purity ceramics with homogeneous distribution of components even on the atomic scale. Among the available materials, metal oxides having the spinel-type structure are often used as model systems since reproducible result, good sensitivity and short response time have been observed with these materials [10]. The measure of the membrane potential is a significant method for characterizing the ion-transport phenomena across a charged membrane [11,12]. Theoretically, the membrane potential in a charged membrane electrolyte solution system developed by Teorell, Meyer, and Sievers (TMS) can be treated by the Donnan equilibrium theory and the Nernst–Planck equation. It is assumed that fixed-charged groups are homogeneously distributed in the membrane and the effect of mean activity coefficient of the electrolyte in external solution is negligible [13]. The ion-transport phenomena across a charged membrane in an aqueous solution system have been studied by many authors [14–16].

In this chapter, a composite titanium–vanadium (1:1) phosphate (TVP) membrane is developed by sol–gel process using polystyrene as a binder. Fixed-charge density, the most effective parameter has been evaluated and utilized to calculate theoretical membrane potentials for different electrolyte concentrations using TMS equation [17–19]. In addition to the fixed-charge

density, distribution coefficient, transport numbers, mobility, charge effectiveness and other related parameters were calculated for characterizing the TVP composite membrane.

4.2 Experimental Method

4.2.1 Preparation of membrane

Titanium–Vanadium (1:1) phosphate precipitate was prepared by mixing a 0.2-mol titanium (III) chloride (Otto Kemi, India with 99.989% purity) and vanadium (III) chloride (Merck, Germany with 99.989% purity) with 0.2-mol tri-sodium phosphate (E. Merck, India with 99.90% purity) solutions. The precipitate was washed properly with deionized water to remove free electrolyte and then dried at 80°C. The precipitate was ground into fine powder and was sieved through 200 mesh (granule size <0.07 mm). Pure crystalline polystyrene (Otto Kemi, India, AR) was also ground and sieved through 200 mesh. The titanium–vanadium (1:1) phosphate along with appropriate amount of polystyrene powder was mixed thoroughly using mortar and pestle. The mixture was then kept into a cast die having a diameter of 2.45 cm and placed in an oven maintained at 200°C for about an hour to equilibrate the reaction mixture [20,21]. The die containing the mixture was then transferred to a pressure device (SL-89, UK), and various pressures such as 80, 100, 120, 140 and 160 MPa were applied during the fabrication of the membranes. As a result titanium–vanadium (1:1) phosphate membrane of approximate thicknesses 0.095, 0.090, 0.085, 0.080 and 0.075 cm were

obtained, respectively. The membranes prepared by embedding 25% of polystyrene by weight were suitable and greater or lesser than this weight did not show reproducible results and appeared to be unstable. Membranes prepared in this way were found stable and further subjected to microscopic and electrochemical examinations for cracks and homogeneity of the surface. Only those membranes which had smooth surface and generated reproducible potentials were assured by carefully controlling the conditions of fabrication.

4.2.2 Scanning electron microscopy (SEM)

The sample prepared at various pressures was heated in the tabular furnace for 3 hours and then cooled. A very thin, transparent polymer glue tape was applied on the sample. The sample was then placed on an aluminum stub of 15-mm diameter. Thereafter, it was kept in a vacuum chamber where the entire plastic foil containing the sample was coated with gold (60-μm thickness) for 5 minutes. The scanning electron micrograph (SEM) of gold-coated specimen was recorded, operating at an accelerating voltage of 10 kV using the SEM (FEI Quanta 200, SEM). The elemental analysis of TVP membrane was characterized by Energy Dispersive X-ray Analysis (EDAX).

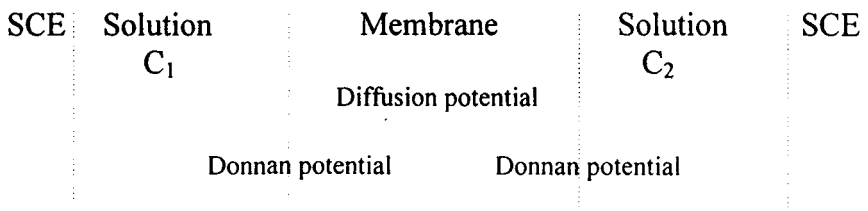
4.2.3 Test Method and Experimental Conditions for Membrane

The membranes were taken in nickel crucible and placed in the furnace for 24 hrs at 200°C, 300°C, 400°C and 450°C and after each sintering, cooled it to room temperature and then morphology of membranes were examined for compaction, crack and swelling by Stereozoom Binocular Microscope 80 X

(Nikon SMZ 1000). The chemical stability of membrane was examined by dipping the freshly prepared membrane individually in increasing strength of solution of harsh chemicals such as $K_2Cr_2O_7$, HNO_3 and H_2SO_4 (up to 1.0 M) in petri dish at 25°C in Digital oven (ACM-111) for 72 hrs and thereafter, the membrane was placed in petri dish contain distilled water for 6 hrs and then dried in oven at 100°C.

4.2.4 Measurement of membrane potential

The freshly prepared charged membrane was installed at the center of a measuring cell, which had a collared glass container on either side of the given membrane. The containers had a hole meant for introducing electrolyte solution and saturated calomel electrodes (SCEs). The half cell contained 25 ml of electrolyte solutions although the capacity of each of the half cells holding the membrane was about 35 ml. Electrochemical cells of the type



were used for measuring membrane potential using Vernier Potentiometer (Osaw, UK) [20,21]. The electrolyte concentration ratio across the membrane was taken as $C_2 / C_1 = 10$, throughout the measurements. The solutions were prepared by using analytical reagent (AR) grade chemicals and ultra pure distilled water. Saturated calomel electrodes were used and were connected to a galvanometer (Osaw, UK). The solutions in both containers were stirred by a

magnetic stirrer to minimize the effects of boundary layers on the membrane potential. The observations were carried out at atmospheric pressure and room temperature.

4.3 Results and Discussion

The thermal and mechanical stability of membranes were carefully examined by investigating the morphology of membrane using the Microscope and SEM images. It was found that the TVP membrane is resistant to compaction i.e., diameter = 2.45 cm and width =0.085 cm remain unchanged, did not found any crack and swelling in sintered membrane up to 400°C. But, a little compaction in membrane was resulted at around 450°C thus; the TVP membrane is thermally and mechanically stable up to 400°C. In addition to this, the observed membrane potential of sintered to unsintered membranes were taken and compared, the analysis of data revealed that an insignificant change in value (±0.1 mV) were obtained which is also supported the thermal and mechanical stability of TVP membrane. The chemical stability of membrane was examined by dipping the membrane in increasing strength of solution of harsh chemical such as $K_2Cr_2O_7$, HNO_3 and H_2SO_4 and compared with the morphology of freshly prepared TVP membrane using Microscope. It is interesting to note that the TVP membrane was resistant to 1.0 M solution of a strong oxidizing agent $K_2Cr_2O_7$ for 72 hrs but higher strength than 1.0 M solution caused a very slow decomposition. It is pertinent to note that the investigated membrane was almost unchanged in; colour, decomposition,

compaction, swelling and crack up to considerable strength of these harsh chemicals. They were stable after long usage, i.e. durable. The binder polystyrene was selected because its cross-linked rigid framework provides an adequate adhesion to the TVP composite, which accounts for the mechanical stability to the membrane. It is thus; a potential candidate for this membrane. Therefore, the TVP composite membrane is better than a conventional membrane which degrades under harsh conditions and often encountered in industrial settings [22]. The characterization of membrane morphology has been studied by using SEM [23,24]. The information obtained from SEM images have provided guidance in the preparation of well-ordered precipitates, composite pore structure, micro/macro porosity, homogeneity, thickness, surface texture and crack-free membranes [25,26]. The SEM surface images of the TVP composite membranes were taken at different applied pressures and are presented in Figure 1. The elemental analysis of TVP membrane was characterized by using EDAX as it is shown that the membrane contains titanium, vanadium and phosphate and the presence of carbon is attributed to polystyrene used as a binder and are presented in Figure 2. The SEM images are composed of dense and loose aggregation of small particles and formed pores probably with non-linear channels are not fully interconnected.

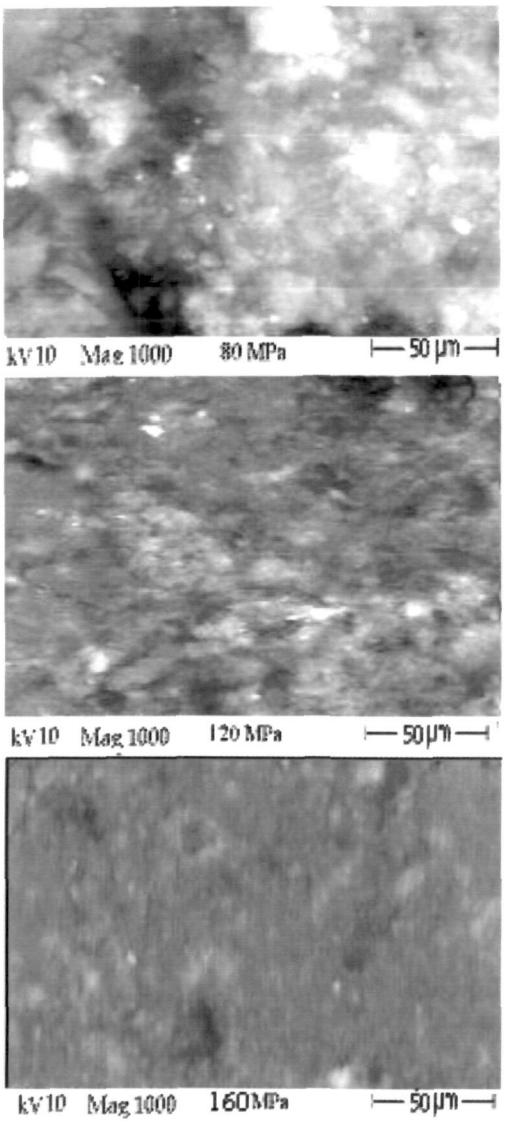


Figure 1. SEM images of polystyrene-based titanium–vanadium phosphate (TVP) composite membranes prepared at different applied pressures of 80, 120 and 160 MPa.

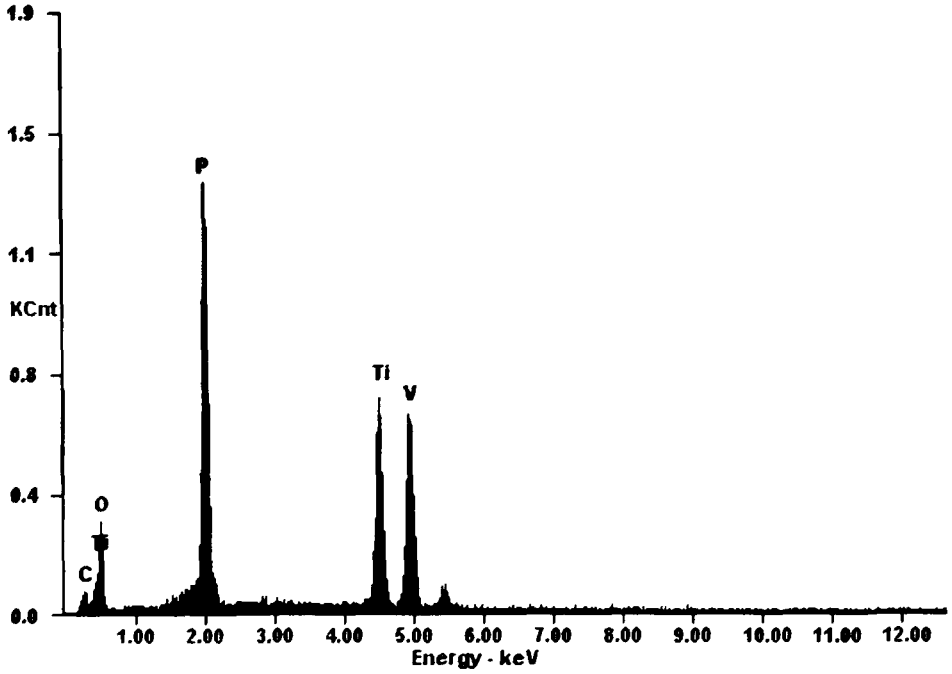


Figure 2. The typical EDAX spectrum for titanium–vanadium phosphate (TVP) composite membranes.

Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various sizes. The surface openings seem to decrease with increasing applied pressure during the fabrication of membranes.

Inorganic composite membranes have the ability to generate potential when two electrolyte solutions of unequal concentration are separated by a membrane and driven by different chemical potential acting across the membrane [27,28]. The electrical character of the membrane regulates the migration of charged species, and diffusion of electrolyte from higher to lower concentration takes place through the charged membrane [12]. The values of membrane potential $\Delta\psi_m$ measured across TVP membranes in contact with various 1:1 electrolyte (KCl, NaCl and LiCl) were dependent on concentration of electrolyte present on both sides of the membrane at 25 ± 1°C and is given in Table 1. The observed potential was low (mV, positive) and found to increase on decreasing the concentration of electrolyte (KCl, NaCl and LiCl) which is a usual behavior of inorganic membranes. The selectivity character of ion–exchange membranes were reported on the basis of membrane potential values, performed on uni-uni and multi-univalent electrolyte as 1:1, 2:1 and 3:1. The reversal in sign from positive to negative values of membrane potential occurred with the 2:1 and 3:1 electrolyte. This is evidently due to the adsorption of multivalent ions, which led to a state where the net positive charge left on the membrane surface made the anion selective with 2:1 and 3:1 electrolyte [29,30]. Thus, the membrane selectivity also depends upon the valence of electrolyte under studies and in our observations with 1:1 electrolyte

Table 1. Observed, theoretical membrane potentials (mV) and charged density across the TVP composite membranes in contact with 1:1 electrolyte solution at different concentrations $C_2/C_1 = 10$ at 25±1° C.

	Applied Pressure (MPa)														
	80			100			120			140			160		
C_2 (mol/l)	Membrane Potential (O)														
	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl
.0001	50.5	51.9	53.0	52.0	52.9	54.0	53.0	53.9	55.1	54.2	55.3	56.8	55.0	56.2	57.3
.0010	46.0	47.1	47.9	47.1	47.9	49.0	48.1	49.2	50.5	49.0	50.4	51.8	50.1	51.3	52.5
.0100	23.5	24.6	26.2	24.6	25.8	26.9	26.0	26.9	28.6	26.5	27.6	28.7	27.6	29.0	31.0
.1000	9.03	10.0	11.1	10.0	11.5	12.5	10.9	11.8	13.4	11.5	12.8	13.6	12.8	14.0	16.0
1.000	6.33	7.30	8.45	7.52	8.50	10.0	8.30	9.55	10.9	9.02	10.0	11.1	10.5	11.9	13.5
	Membrane Potential (T)														
.0001	58.94	58.94	58.94	59.01	59.01	59.01	59.12	59.12	59.12	59.14	59.14	59.14	59.16	59.16	59.16
.0010	47.25	47.25	47.25	49.57	49.57	49.57	54.48	54.49	54.48	55.90	55.90	55.90	56.78	56.78	56.78
.0100	11.46	11.48	11.50	13.45	13.46	13.48	20.41	20.42	20.44	24.02	24.03	24.05	27.14	27.15	27.17
.1000	1.337	1.351	1.378	1.567	1.582	1.609	2.489	2.503	2.530	3.063	3.077	3.103	3.634	3.649	3.675
1.000	0.253	0.274	0.297	0.277	0.297	0.320	0.369	0.390	0.412	0.427	0.448	0.470	0.485	0.505	0.528
	Charged Density $\overline{D}$ (eq/l)														
	1.24	1.00	0.79	1.52	1.31	1.09	3.87	3.41	2.11	5.44	4.04	2.94	8.59	5.61	3.34

found to be positive value of membrane potential throughout for TVP composite membranes (Table 1). Therefore, the TVP composite membrane shows the cation–selective behavior for various 1:1 electrolyte solutions. The membrane potential was also seen to be largely dependent on the pressure applied during the membrane fabrication. Application of higher pressure at TVP composite membranes led to reduction in their thicknesses, contraction in pore volume and consequently offered a progressively higher fixed-charge density [11,31]. This, in turn, led to a higher membrane potential, which can be analyzed from Table 1.

The surface-charge model works as a tool to improve the performance of the membrane filtration process. The charge property of the membrane matrix greatly influences by the counter-ion than co-ion as well as the transport phenomena in the solutions. The surface-charge concept of the TMS model for charged membrane is an appropriate starting point for the investigations of actual mechanisms of ionic or molecular processes, which occur in membrane phase [17–19]. The TMS model assumes uniform distribution of surface-charge and consists of Donnan potential and diffusion potential at the two solution membrane interface arising from unequal concentrations of the mobile ions.

According to the TMS, the membrane potential $\Delta\overline{\Psi}_m$ is applicable to an idealized system and is given by

$$\Delta\overline{\Psi}_m = 59.2\left(\log\frac{C_2}{C_1}\frac{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}}{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}}+\overline{U}\log\frac{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}\,\overline{U}}{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}\,\overline{U}}\right), \qquad \overline{U} = (\overline{u}-\overline{v})/(\overline{u}+\overline{v})$$

(1)

where $\overline{u}$ and $\overline{v}$ are the ionic mobilities ($m^2/V/s$), of cation and anion, respectively, in the membrane phase. The charge densities of inorganic membranes were estimated from the membrane potential measurement and can also be estimated from the transport number. From the plots in Figure 3 (a, b and c), the charge density parameter can be evaluated for a membrane carrying various charge densities, $\overline{D} \leq 1$ for different 1:1 electrolyte systems. The theoretical and observed potentials were plotted as a function of $-\log C_2$ as shown in Figure 3 (a, b and c). Thus, the coinciding curve for various electrolyte systems gave the value for the charge density $\overline{D}$ within the membrane phase. The microstructure of dense and loose aggregation of small particles, which form the interconnected channels and pores, appeared to be more compact. The structure is arranged in order with successive increase in pressure, which can also be seen in the SEM (Figure 1). Therefore, the increase in the values of $\overline{D}$ with higher applied pressure is due to successive increase of charge per unit volume as well as the modification in the surface microstructure of the TVP membrane. Most of the fixed-charge groups exist near membrane surface region and hence, a fixed-charge density appeared to decrease from the membrane surface to the membrane interior [32].

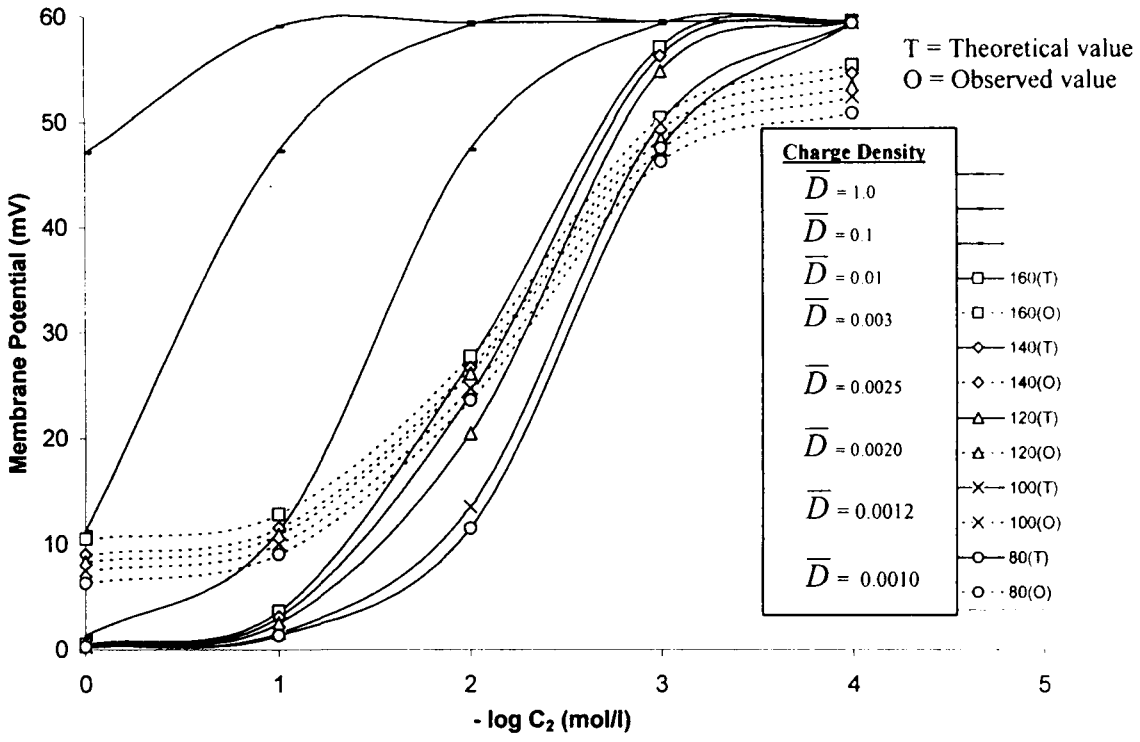


Figure 3 (a). Plots of membranes potential (mV) versus $-\log C_2(\text{mol/l})$ at different concentrations of KCl electrolyte solution for titanium–vanadium phosphate (TVP) membranes prepared at different pressures of 80–160 MPa.

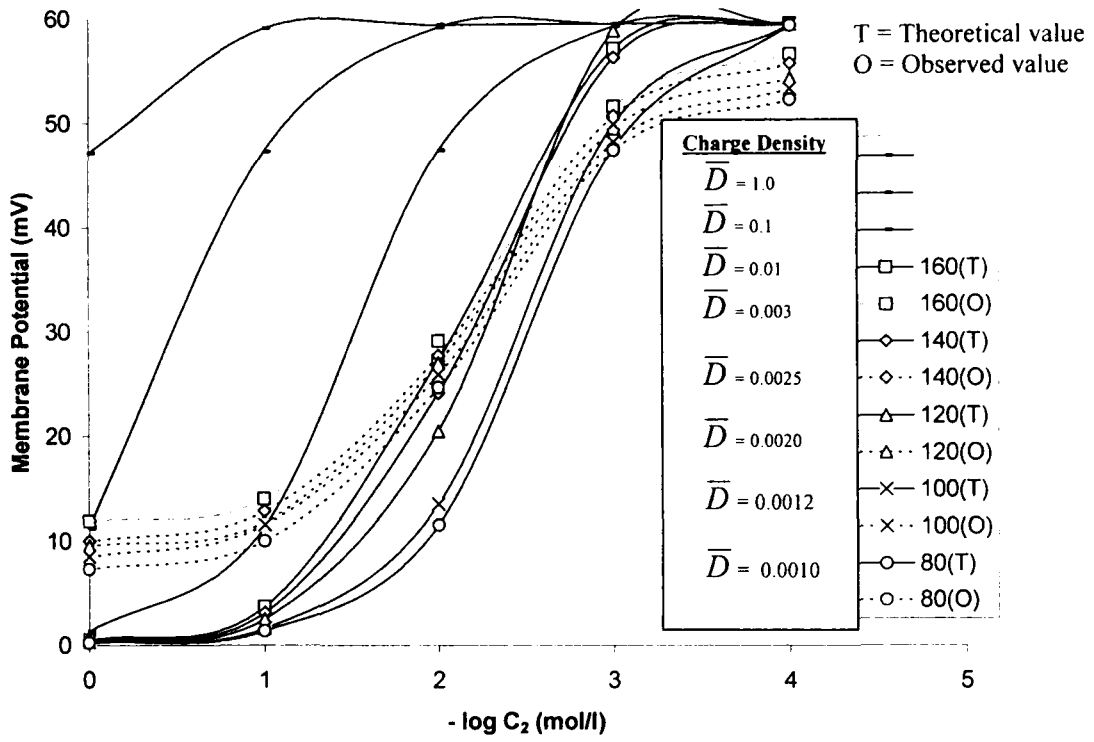


Figure 3 (b). Plots of membranes potential (mV) versus $-\log C_2$(mol/l) at different concentrations of NaCl electrolyte solution for titanium–vanadium phosphate (TVP) membranes prepared at different pressures of 80–160 MPa.

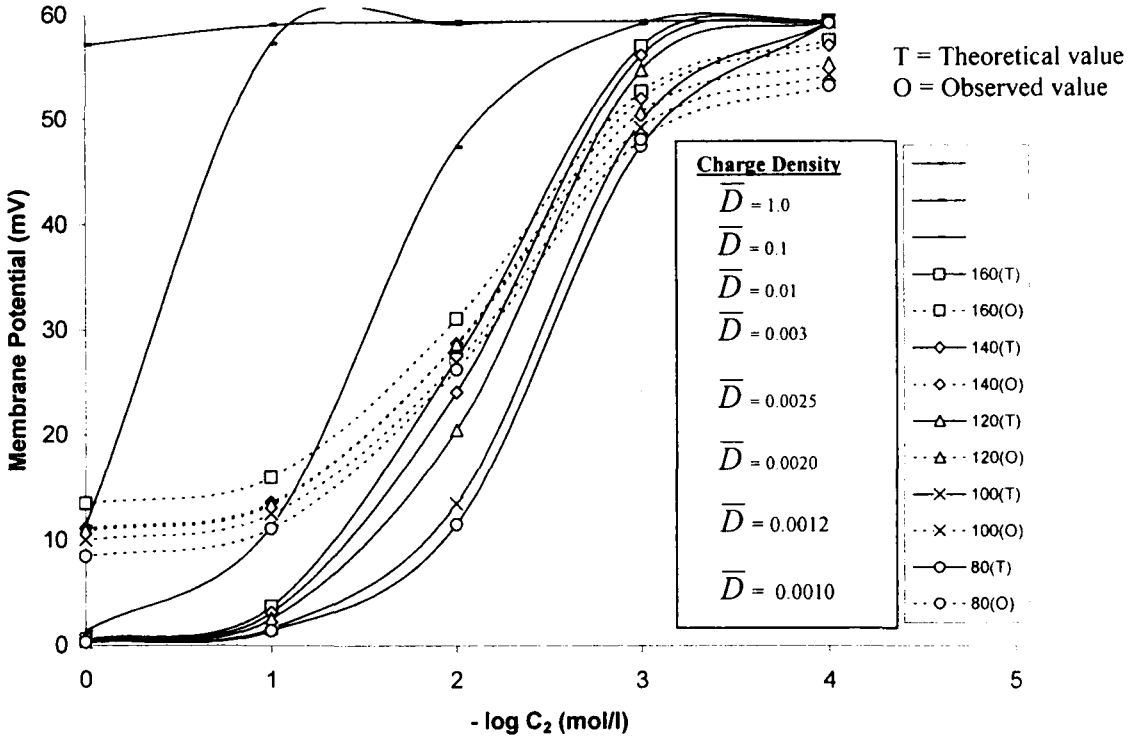


Figure 3 (c). Plots of membranes potential (mV) versus $-\log C_2(\text{mol/l})$ at different concentrations of LiCl electrolyte solution for titanium–vanadium phosphate (TVP) membranes prepared at different pressures of 80–160 MPa.

The plots of surface charge density $\overline{D}$ of the membrane for 1:1 electrolyte (KCl, NaCl and LiCl) versus pressures is shown in Figure 4. The values of charge density increased gradually and were coincident up to 100 MPa pressure for used electrolyte. Thereafter, a sharp deviation in charge density was observed with increasing the applied pressure. The value of the charge density $\overline{D}$ ranges from 0.79–8.59 eq/l. The charge density of various electrolyte is found to be in order of KCl>NaCl>LiCl throughout the range of applied pressure at which the membranes were prepared. When the value of charge density of the TVP composite membrane was compared with those of commercially available *Dowex-50* membranes for various electrolyte (KCl, NaCl and LiCl), it was found that the charged density of the TVP composite membrane is greater by several folds than that of *Dowex-50* membranes [33]. These results indicate that the charge model may work as a tool to improve the performance of the membrane filtration process. Since, the charge density is an important parameter governing transport phenomena and the charge property of the membrane dominates the electrostatics interaction between the membrane and particles in the feed solution due to the prefential adsorption of some ions. Therefore, by controlling the solution physico-chemistry, the optimum charge property of the membrane can be obtained as desired [34]. The TMS Equation (1) can also be expressed by the sum of Donnan potential $\Delta\Psi_{Don}$ between membrane surfaces and external solutions and the diffusion potential $\Delta\overline{\Psi}_{diff}$ within the membrane [35,36].

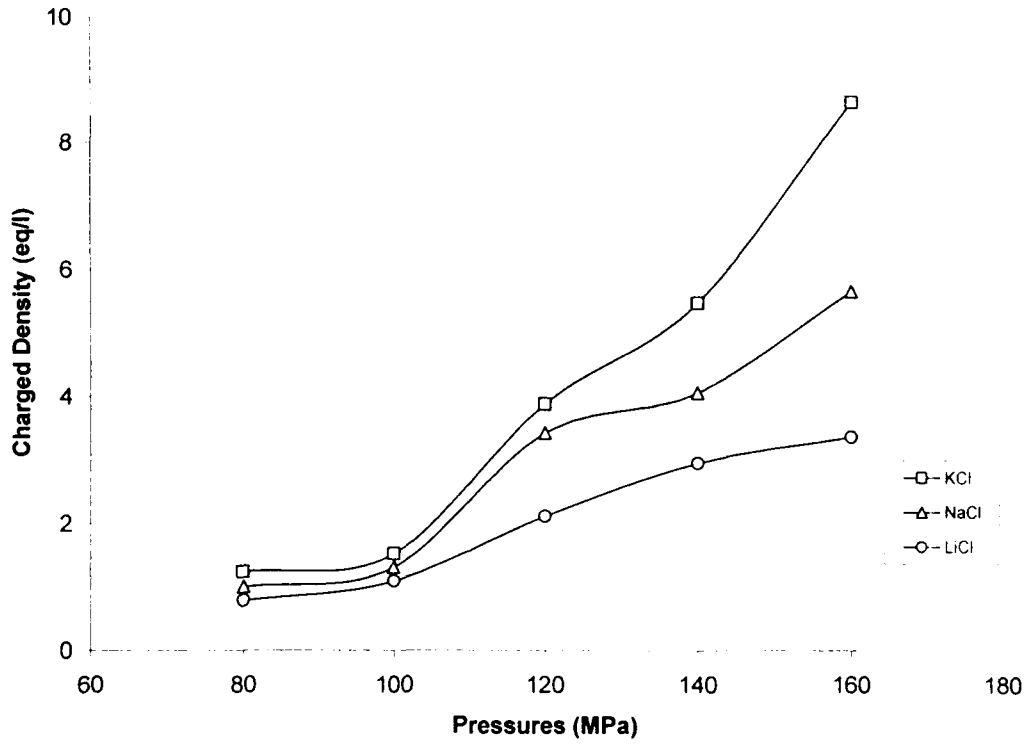


Figure 4. Plots of fixed-charge density (eq/l) $\overline{D}$ versus pressures (80–160 MPa).

$$\Delta\overline{\Psi}_m = \Delta\Psi_{Don} + \Delta\overline{\Psi}_{diff} \tag{2}$$

$$= -\frac{RT}{V_k F}\ln\left(\frac{\gamma_{2\pm}C_2\overline{C}_{1+}}{\gamma_{1\pm}C_1\overline{C}_{2+}}\right) - \frac{RT}{V_k F}\frac{\overline{\omega}-1}{\overline{\omega}+1}\times\ln\left(\frac{(\overline{\omega}+1)\overline{C}_{2+}+(V_x/V_k)\overline{D}}{(\overline{\omega}+1)\overline{C}_{1+}+(V_x/V_k)\overline{D}}\right) \tag{3}$$

The R, T and F have their usual significance; $\gamma_{1\pm}$, $\gamma_{2\pm}$ are the mean ionic activity coefficients; $\overline{\omega} = \frac{\overline{u}}{\overline{v}}$ is the mobility ratio of the cation to the anion in the membrane phase and $\overline{C}_{1+}$ and $\overline{C}_{2+}$ are the cation concentrations in the membrane phase first and second, respectively. The cation concentration is given by the equation

$$\overline{C}_+ = \sqrt{\left(\frac{V_x\overline{D}}{2V_k}\right)^2 + \left(\frac{\gamma_\pm C}{q}\right)^2} - \frac{V_x\overline{D}}{2V_k} \tag{4}$$

Here V_k and V_x refer to the valency of cation and fixed-charge group on the membrane matrix, q is the charge effectiveness of the membrane and is defined by the equation

$$q = \sqrt{\frac{\gamma_\pm}{K_\pm}} \tag{5}$$

where $K_\pm$ is the distribution coefficient. It is expressed as

$$K_\pm = \frac{\overline{C}_i}{C_i}, \qquad \overline{C}_i = C_i - \overline{D} \tag{6}$$

where $\overline{C}_i$ is the ith ion concentration in the membrane phase and C_i is the ith ion concentration of the external solution. The transport properties of the membrane in various electrolyte solutions are important parameters for further investigation of the membrane phenomena as given in Eq. (7).

$$\Delta\overline{\psi}_m = \frac{RT}{F}(t_+ - t_-)\ln\frac{C_2}{C_1}, \quad \frac{t_+}{t_-} = \frac{\overline{u}}{\overline{v}} \tag{7}$$

Eq. (7) was first used to calculate the values of transport numbers t_+, mobility ratio $\overline{\omega} = \frac{\overline{u}}{\overline{v}}$ and finally $\overline{U}$ as given in Table 2. The values of mobility $\overline{\omega}$ of the electrolyte in the membrane phase were found to be high at lower concentration of all the electrolyte (KCl, NaCl and LiCl). Further increase in concentration of the electrolyte led to a sharp drop in the values of $\overline{\omega}$ as given in Table 2. The high mobility is attributed to higher transport number of comparatively free cations of electrolyte and also be similar trend as the mobility in least concentrated solution. The values of the parameters $K_{\pm}$, q and $\overline{C}_+$ derived for the system have also been included in Table 2. Using Eq. (6) it was found that the values of distribution coefficients increased at lower concentration of electrolyte. As the concentration of electrolyte increased, the values of distribution coefficients sharply dropped and, thereafter, a stable trend was observed as shown in Table 2. The large deviation in the value of $K_{\pm}$ at the lower concentration of electrolyte was attributed to the high mobility of comparatively free charges of the strong electrolyte and thus, reached into the membrane phase easily compared to higher concentrated electrolyte solution.

The charge effectiveness q, values for KCl are the smallest of the electrolyte used in this study and order is KCl < NaCl < LiCl. The effective charge density estimated by the ionic transport procedure depends upon the ionic radii and valence of the counter-ions; several authors have found that

Table 2. The values of t_+, $\overline{U}$, $\overline{\omega}$ and $K_\pm$, q, $\overline{C}_+$ evaluated from using Eq. (9) and Eqs. (4)–(6) respectively, from observed membrane potentials for various electrolyte at different concentrations for TVP composite membranes prepared at 120 MPa pressure.

KCl (Electrolyte)						
C_2(mol/l)	t_+	$\overline{U}$	$\overline{\omega}$	$K_\pm$	q	$\overline{C}_+$
.0001	0.94	0.88	15.7	37.70	0.162	0.00001
.0010	0.90	0.80	9.00	2.870	0.579	0.00021
.0100	0.71	0.42	2.45	0.613	1.212	0.00361
.1000	0.59	0.18	1.44	0.961	0.894	0.08040
1.000	0.57	0.14	1.33	0.996	0.780	0.77113
NaCl						
.0001	0.95	0.90	19.0	33.10	0.173	0.00002
.0010	0.91	0.82	10.1	2.410	0.633	0.00021
.0100	0.72	0.44	2.57	0.659	1.170	0.00413
.1000	0.60	0.20	1.50	0.965	0.897	0.08176
1.000	0.58	0.16	1.38	0.996	0.811	0.80377
LiCl						
.0001	0.96	0.92	24.0	20.10	0.223	0.00002
.0010	0.92	0.84	11.5	1.110	0.932	0.00015
.0100	0.73	0.46	2.71	0.789	1.070	0.00585
.1000	0.61	0.22	1.56	0.978	0.898	0.08486
1.000	0.59	0.18	1.44	0.997	0.881	0.87538

the effective charge density increases with increasing the adsorption of co-ion of electrolyte solutions for charged membranes. The counter-ions Cl^-, is the same for all the electrolyte used therefore, the variation of charge effectiveness values are possibly due to increase in adsorption of co-ions on charged membrane and their order is $K^+ < Na^+ < Li^+$ and follow the similar trend for the charge effectiveness [37,38]. The membrane potentials using TMS equation and the observed membrane potentials at different concentrations for various electrolyte systems have been compared and provided in Figure 5. It can be found that the theoretical lines agree well with the experimental lines in the lower concentration region while the obvious deviations exist between the theoretical and experimental lines at higher concentration. One of the reasons is that the mean activity coefficients of the electrolyte do not equal unity, especially in the high concentration regions, so the amount of ion-pairs in the external solutions will increase as well as non-ideality caused the deviation to be more in high concentration region [36]. These effects are often simultaneously present in the charged membranes which was explained in the previous chapter.

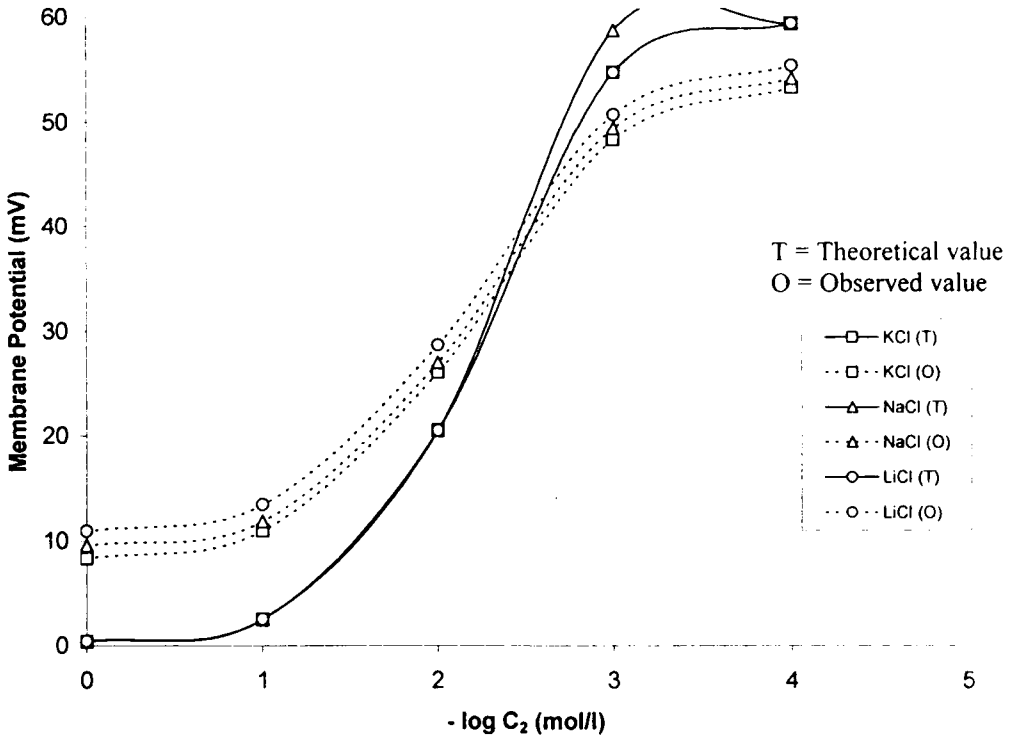


Figure 5. Membranes potential across titanium–vanadium phosphate (TVP) membranes using various electrolyte (1:1) solutions at different concentrations.

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CONCLUSION

The polystyrene-based titanium phosphate, vanadium phosphate and titanium–vanadium phosphate composite membranes were prepared by sol–gel process and found that they are quite stable and did not show any dispersion in water and in other electrolyte solutions. Polystyrene is suitable binder because of its cross-linked rigid framework which provides an adequate adhesion to the membrane. SEM images have provided guidance in the preparation of well-ordered precipitates, composite pore structure, micro/macro porosity, homogeneity, thickness, surface texture and crack-free membranes. The thermal and mechanical stability of membranes were carefully examined by investigating the morphology of membranes using the Microscope and SEM images. It was found our investigated membranes were thermally, mechanically as well as resistant to harsh chemical up to considerable range. Therefore, these are stable after long usage, i.e. durable. The membrane potentials of inorganic membranes were measured with uni-univalent electrolyte (KCl, NaCl and LiCl) solution using saturated calomel electrodes (SCEs). The membrane potential offered by electrolytes is in the order of LiCl > NaCl > KCl and the obtained data indicates that the behaviour of investigated membranes is cation–selective. Fixed-charge density is the central parameter governing transport phenomena in membranes and depends upon the feed composition and applied pressure and also on the prefential adsorption of some ions of electrolyte on membrane surface. The fixed-charge concept of TMS model for charged membrane is an appropriate starting point for the investigations of the actual mechanisms of ionic or molecular processes which

occur in membrane phase. The charge densities of inorganic membranes were estimated from the membrane potential measurement and can also be estimated from the transport number. To evaluate this parameter for the simple case of a 1:1 electrolyte and a membrane carrying various charge densities $\overline{D} \leq 1$. The theoretical and observed potentials were plotted as a function of concentrations. Thus, the coinciding curve for various electrolyte systems gave the value for the charge density $\overline{D}$ within the membrane phase. The surface charge density $\overline{D}$ of these membranes is found to depend on the applied pressure to which the membrane was subjected to its initial stage of preparation. It was observed that membranes prepared at lower pressure have low fixed-charge density whereas membrane prepared at high pressure carry higher charge-density and essentially wider and narrow surface openings respectively. The surface-charge model works as a tool to improve the performance of the membrane filtration process. The charge property of the membrane matrix greatly influences by the counter-ion than co-ion as well as the transport phenomena in the solutions. In addition to the evaluation of surface-charge density, transport numbers, mobility, distribution coefficient, charge effectiveness and other related parameters were calculated for characterizing the prepared membranes. The experimental results were analyzed on the basis of TMS approach and it was found that the calculated values agree well with the experimental results.